STUDIES ON
COORDINATION COMPOUNDS
OF SOME GROUP 13 & 15 ELEMENTS

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Dedicated

To My

Parents who always

inspire me !!

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Certificate

This is to certify that the thesis entitled "**STUDIES ON COORDINATION COMPOUNDS OF SOME GROUP 13 & 15 ELEMENTS**" describes the original work carried out by Mr. Rajnish Rai under my supervision for the award of the degree of Doctor of Philosophy of the University of Allahabad, Allahabad and that the work reported in this thesis has not been submitted to any University for the award of a Diploma or a Degree.

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INTRODUCTION

1.1 The Main Group Elements

General Characteristics

The s and p-block elements taken together are known as main group elements as such they include the elements belonging to group 1-2 and group 13-18. The elements belonging to group 1 and 2 which have one or two electron in their outermost s orbitals proceded by noble gas configuration are known as s-block elements whreas the p-block elements have electronic configuration ns^2np^{1-6}.

s-Block Elements		p-Block Elements					
1	2	13	14	15	16	17	18
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr
Rb	Sr	In	Sn	Sb	Te	I	Xn
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
Fr	Ra						

General Features of s-Block elements

☞ These are metals having electropositive character, soft silvery white colour.

☞ They have low melting and boiling points because of low binding energy.

☞ They have low ionization energies.

☞ It is the most characteristic chemical property that they show constant oxidation number.

☞ The s-blcok elements are powerful reducing agents.

General Features of p-Block Elements

The p-block elements are divided in three categories

(a) The non metal or electronegative metal in group '13' except Aluminium; in group '14' except Germanium, Tin, Lead; in group '15' except Arsenic, Antimony; in group '16' except Tellurium, Polonium and all the elements of group '17'.

(b) The metalloids or the elements of intermediate character between electropositive and electronegative. These are Aluminium, Germanium, Tin, Lead, Arsenic, Antimony, Tellurium and Polonium.

(c) Rest of the elements are metallic in nature.

2. The p-block elements do not form simple cations except when inert pair effect operates. These elements show variable oxidation states differ only by two units for example $Tl^{+} \rightarrow Tl^{+1}$, $Sn^{+2} \rightarrow Sn^{+4}$, $Sb^{+3} \rightarrow Sb^{+5}$, $Pb^{+2} \rightarrow Pb^{+4}$.

3. They form covalent compounds.

4. The oxides of most of the electronegative elements are all acidic. The oxides of metalloids are amphoteric.

In main group elements we have special interest in group '13' and '15' elements. The metals have tendency to loose electron to form positive ion. This tendency is known as metallic character.

$$M \rightarrow M^{+} + e$$

In group '13' elements the metallic character increases from Boron to Aluminium while Boron is regarded as semi-metal whereas Aluminium is regarded as metalloid. In the group '15' elements the metallic character increases from top to bottom with increase in atomic number Arsenic and Antimony are metalloids, while last element Bismuth is metal.

In group '13' density increases on moving down the group but Aluminium has exceptionally low density. The melting point decreases considerably up to Gallium. In group '15' elements melting (except for antimony and bismuth) and boiling point increases with increase in atomic number. Melting point of Bismuth is unusually low.

The group '13' elements having valence shell electronic configuration ns^2np^1 show constantly +3 and +1 oxidation states. The +1 oxidation state becomes more stable in heavier elements due to inert pair effect. The group '15' elements having electronic configuration ns^2np^3 show two positive oxidation states +3 and +5; for example this group forms two types of oxides M_2O_3 and M_2O_5. The +3 state becomes more and more stable on moving down the group from Phosphorus to Bismuth.

Since ionization energies decrese on moving down the group it is evident that reducing character in a given group increases with increase in atomic number conversely oxidising character of elements in a group decreases with increse in atomic number.

1.2.1 General Chemistry of Aluminium

The name of Aluminium derived from double sulfate $K.Al(SO_4)_2 12H_2O$ which is medicinally used as astringent in ancient

Greece and Rome. The name proposed by Humphry Davey in 1925 in North America where ACS decided "Aluminium" in its publications.

Table -1 Physical Properties of Aluminium

Properties	Values
Atomic number	13
Atomic weight	26.98
Electronic configuration	[Ne] $3s^2 3p^1$
Density (g/cm^3)	5.9
Melting point	640.45
Boiling point	2520
Ionization nergy (KJ mol^{-1})	
Firt	577.5
Second	1816.7
Third	2744.7
Metal radius / pm	143
Ionic radius / pm	53.5

Pure Aluminium is silvery white metal with many desirable properties. It is light weight, non toxic pleasing appearance. It has high thermal and elctrical conductivity.

Aluminium is second malleable metal than gold and sixth position having ductibility. It is used as reducing agent for production of certain metals like chromium and maganese. The oxidation of Aluminium enromus quantities of heat produced. It is used in the Thermit welding of metal. Aluminium is unattcked by nitric acid it is

used in chemical plants and also for transporting nitric acid.

Table -2 Oxidation states and steriochemistries of group 13 elements.

Oxidation State	Coordination Number	Geometry	Examples
+1	6	Distorted Octahedral	TlF
+2	4	Tetrahedral	$[AlBr(NEt_3)]_4,[Ga\{CH\{(SiMe_3)_2\}]_4$
	4	Tetrahedral	$[Ga_2Cl_6],[In_2Cl_6]^{2-}[Al(Bt_1)_2PhoMe_2]$
	3	Trigonal	$[Al_2\{Ch(SlMe_3)_4\}]$
+3	3	Planar	$In[Co(CO)_4],[Al(mes)_3]$
	4*	Tetrahedral	$[AlCl_4],[GaH_4],[Al_6(CH_3)_6],[Ga_2Cl_6]$
	5	Trigonal bipyramidal	$[AlCl_3(NMe)_2], [In(NCS)_5]_4[(Me)_2$ $Ga(CI)(Phen)],[InCl_5(PPh_3)_3]$
		Square pyramidal	$[(Et)(Al(Salen)],[(p\text{-}Tolyl)Tl(S_2CNEt_2)]$
	6	Octahedral	$[Al(H_2O)_6]^{+3},[Ga(acac)_3],[AlF_6]^{-3},$
	8	Dodecahedral	$[Al(BH_4)_4]^-$

* Most Common Oxidation State

The crystal structure of Aluminium is face centered cubic, typical of many metals, in which each aluminium atom is surrounded by 12 nearest neighbours at 286 pm. Al^{+3} is completely harmless and non toxic to humans. $Al(OH)_3$ is widely used for anti-acid treatment for indigestion. Aluminium is acutly toxic to patients suffering from renal problems because they cannot excrete Aluminium. The patentics of Alzheimer disease have deposit of Aluminium salt in brain.

Anhydrous Aluminium salt can not be prepared by heating hydrate for reasons closely related to the amphoterism and hydrolysis of such compounds, for example $AlCl_3 6H_2O$ in reality is $[Al(H_2O)_6]$ the Al-O interaction percludes formation of Al-Cl bond.

$$2[Al(H_2O)_2] \, Cl_3 \xrightarrow{\text{Heat}} Al_2O_3 + 6HCl + 9H_2O$$
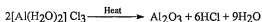
The alkoxide group (OR) usually acts as bridging ligand. Although the degree of association of group '13' alkoxide is controlled by size of R.

$$Al + 3ROH \xrightarrow[\text{Catlyst Warm}]{1\%HgCl_2 \text{ as}} Al(OR)_3 + ^3/_2 \, H_2$$

$$AlCl_3 + 3RONa \longrightarrow Al(OR)_3 + 3NaCl \downarrow$$
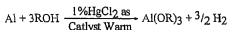
The aluminium isopropoxide is important because it is used in organic synthesis for the reduction of ketrones. Aluminium alkoxide can be prepared by above reactions.

The aluminium β-diketonates have been much studied by nmr methods because of their steriochemical non-rigidity. Aluminium (III) forms stable complexes with di, tri and hexadentate chelating ligands in which metal is octahedrally coordinated.

1.2.2 Chemistry of Antimony

Antimony compounds were also known to the ancients, the black sulfide, stibnite was used early biblical times as cosmetics. The name stiblium was given by Pliny while the name antimonium was given by Jabir.

The elements As, Sb and Bi are not very abundent. Their most important source is sulphides occurring as traces in other ores. They are well known because they are obtained metallurgical byproducts from roasting of sulphide ore and obtained as metallurgical byproducts from roasting of sulphide ores in smelter.

Table - 3 Physical Properties of Antimony

Properties	Values
Atomic number	51
Atomic weight	121.76
Electronic Configuration	$[Xn]\ 5s^2\ 5p^3$
Density (g/cm^3)	41.7
Melting point	1753
Boiling point	6.684
Covalent	630.7
Ionization energies (KJ mol^{-1})	
First	0.834
Second	1.595
Third	2.443
Radii (A°)	0.92 (Sb^3)
Ionic	1.41

Antimony obtained as Sb_2O_3 in the flue dust from roasting of ZnS ores. This is easily reduced with metal and carbon. The most important ore of antimony is stilbnite Sb_2S_3. The metal is obtained by fusing it with iron.

$$Sb_2S_3 + 3Fe \longrightarrow 2Sb + 3FeS$$

The semiconductor grade Antimony is prepared by chemical reduction of highly purified compounds. AlSb, GaSb and InSb have applications in infrared devices, diodes and Hall effect devices, ZnSb has good thermo-electric properties. Antimony is also used in alloys with Sn and Pb. It is also used to electroplate steel to prevent rusting. Antimony compounds are used as fire retardants in foam filling for furniture and mattresses.

Table - 4 Major Steriochemical Pattern of Group '15' Elements

Oxidation State	Coordination Number	Geometry	Examples
1	3	Trigonal Planar	$PhP[Sb_4(CO)_3CP]$
	2	Angular	$Ph^{2-}, (Me_3N_2P^+, R_3N-P=NR_3$
	3	Pyramidal	$PH_3, AsH_3, SbPh_3$
	4	Tetrahedral	$PH_4, P(CH_2OH)_4, AsPh_4^+$
	5	Trigonal bipyramidal	$KSb_2F_5, SbCl_5(PhNH_2)$
	6	Octahedral	$K_3[Sb_2(tart)]_3 3H_2O SbOBOCl$
	6	Octahedral	$[BeF_4O_4(OH)_3], [Sb(Br)_6]^{3-}$
	3	Square Planar	$p[N(SiMe_3)_2] (NSiMe_3)_3$
	4	Tetrahedral	$PCl_4^+, (RO)_3PO, RPO(OH)_2$
	5	Trigonal bipyramidal	$AsF_5, AsF_5, SbCl_5, SbPH_5$
	6	Octahedral	$PF_6, Sb(OH)_6, Sb(BR)_6$

The Antimony (III) chloride form complexes with neutral donor atoms. The Sb-N bonds are weak and the lone pair is steriochemically active. The antimony trichloride also forms 1:1 and

1:2 complexes with aromatic hydrocarbon such as naphthalene or p-xylene where weak intraction between $SbCl_3$ and π electrons cloud may occurs.

Antimony has some definite chemistry only in trivalent state. The basic character of Sb_2O_5 being negligible cationic compound of Sb(III) are mostly of "Antimonyl" ion SbO^+ although some of Sb^{+3} ion such as $Sb_2(SO_4)_3$ are known. Antimony salts readily forms complexes with various acids.

1.3 LITERATURE REVIEW

Schiff bases play vital role in the field of coordination chemistry due to preparative accessibility, diversity and structural variability [1]. The chelating properties of Schiff bases have been well described by Holmes and Co-workers [2]. They have high reactivity and specificity and number of applications in industry, agriculture, medicine and inorganic analysis [3,4]. The synthesis of macrocyclic ligands have also been employed. These ligands evoked attention of scientists and have extensively studied because of their relevance to naturally occurring systems [5].

Schiff bases have been used in sterioselective polymerization [6] and various tetradentate Schiff base complexes of Aluminium have been used as catalyst for synthesis [7]. The effect of Schiff base metallo complexes on corrosion of mild steel have also been [8] investigated. These Schiff base complexes adsorbed on surface of

mild steel to prevent corrosion. The sulphur donor Schiff base complexes show antifertility activity in male albino rats [9]. The Schiff base complexes derived from substituted amino anthraquinones and salicylaldehyde used as fluorescence based corrosion indicator. [10]

The Schiff bases derived from, thiosemicarbazones and hydrazones were found to possess tuberculostatic, antibacterial, nematocidal and pesticidal activities. Their antifungal activities are due to presence of toxophorically important >NC=S moiety [11]. Thiosemicarbazides and thiosemicarbazones have aroused special interest due to their activity against viruses, protozoa, small pox and certain kind of tumour [12].

The main group metal complexes derived from Schiff bases containing nitrogen and oxygen find many industrial and medicinal importance]. Schiff bases have gained additional importance due to the synthesis of macrocyclic ligands. The Schiff base comlexes show invitro antitumour activities against cancer cells. The Schiff base complexes also show antibacterial and insecticidal activity.

The Schiff bases have been accompanied by the elemination of one molecule of water from aldehyde or ketone and primary amine. Schiff bases obtained from aldehydes are known as aldimines and those from ketones are known as ketimines. They have general

structure R–CH=N–R or (R₂)C=N–R; where R is alkyl, cycloalkyl, aryl or hetrocyclic radicals.

$$R-CHO + H_2N-R \longrightarrow R-CH=NR + H_2O$$

Such condensation products are commonly known as "Schiff bases". The reaction employed in two steps. First step is marked by formation of addition compound. The second step consists of the splitting of one molecule of water.

The first Schiff base was synthesised from salicylaldehyde and aniline and its methyl derivatives. The product was studied by several workers [8-12]. The presence of azomethine nitrogen at appropriate position lead to the formation of five or six membered ring on complexation.

The mixed ligand complexes [13] of Aluminium with isatin-3-oxime derivative were prepared by Aluminum isopropoxide and salicylaldehydeaniline, and aluminum isopropoxide with (bis salicylidene) ethylenediamine with isatin-3-oxime. These complexes were characterized by spectral studies and reveal that formation of octahedral complexes may occur.

The mixed ligand homo- and hetero-metallic compounds of Gallium [14] were synthesized by equimoleculerar reactions of mononuclear Schiff base complexes, Ga(L)(LH) (LH₂ = HOC₆H₄CMe: NCH₂CHMeOH) andGa(L₄)(L₂)(OGOH) (L₄H=Me₂CHCH₂N:CHC₆H₄OH, L₂H=HOCMe:CHCMe:

NCH_2CH_3, and $HOGOH=HOCMe_2CH_2CHMeOH)$, with isopropoxides of aluminum and boron. These derivatives, $Ga(L)_2B(OPr^i)_2$, $Ga(L)_2Al(OPr^i)_2$, $Ga(L_1)_2OGOB(OPr^i)_3$ and $Ga(L_1)(L_2)OGOAl(OPr^i)_2$, were characterized by elemental analysis, molecular weight measurements and spectral [IR, NMR (^1H ^{13}C, ^{11}B and ^{27}Al)] studies.

Mixed ligand aluminum complexes containing a glycol moiety and bifunctional tridentate Schiff bases were synthesized by different routes. Equimolecularer reactions of $Al(OPr^i)_3$, glycol and substituted benzothiazoline give mixed ligand glycolate derivatives of aluminium $[OGOAl(OH)C_6H_3XC(R):NC_6H_4S]$. But reactions of $(L)Al(OPr^i)$ with $G(OH)_2$ yield different complexes, $[HOGOAlOC_6H_3XC(R):NC_6H_4S]$, where $G=G_1=(-CMe_2CH_2CHMe-)$ or $G_2=(-CMe_2CMe_2-)$; $R=X=H$ (L_1H_2); $R=CH_3$, $X=H$ (L_2H_2); $R=H$, $X=OCH_3$ (L_3H_2). All these derivatives were characterized by elemental analyses, molecular weight measurements and by IR and NMR (^1H, ^{13}C and ^{27}Al) spectral studies [15].

The [16] heteronuclear derivatives of boron were prepared by the equimolecularer reactions of mononuclear boric esters of 2-hydroxyazomethines, $B(2-OC_6H_4CR_1$: $NCH_2CHRO)(2-OC_6H_4CR_1$: $NCH_2CHROH)$ [where R, R'=H, Me,] with isopropoxides of aluminum, titanium and niobium. Diisopropoxy aluminum derivative of ligands shown as and similar triisopropoxytitanium and tetraisopropoxyniobium complexes of the ligand were prepared. All these derivatives were characterized by elemental analysis, molecular

weight measurements and spectral [IR, NMR (^{1}H, ^{13}C, ^{11}B and ^{27}Al)] studies.
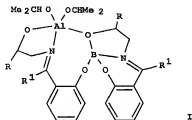
Fig. - 1 : Heteronuclear derivatives of boron

Starting from 3-(4-hydroxyphenyl)propanoic acid, formylation ortho to the phenol and condensation with ortho-aminophenol gave a functionalized Schiff-base ligand. Formation of the N-hydroxysuccinimidyl ester and non-aqueous complexation with AlEt$_2$Cl gave a fluorescent biolabel of Aluminium (III) complexes [17].

The sterically hindered Schiff bases tbm salenH [N,N'-1,2-ethylenebis(3-tert-butyl-5-methylsalicylideneimine)] and tbmsalcenH [N,N'-trans-1,2-cyclohexanediylbis(3-tert-butyl-5-methylsalicylideneimine)] afforded Al complexes [Al(tbmsalen)X] and [Al(tbmsalcen)X] (X = Cl, Me, Et). The molecular structure of [Al(tbmsalcen)Cl].CH$_2$Cl$_2$ was determined by single-crystal x-ray structural analysis which revealed a five-coordinate Al center with a distorted square pyramidal geometry. The alkyl complexes catalyzed the ring-opening

polymerization of ε-caprolactone [18].
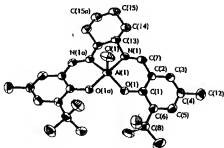
Fig. - 2 : Structure of Schiff base complex [(salen)(tBu)Al]₂O

The Schiff base ligands [3,5-But2-2-(OH)C₆H₂CH:NL] [L = CH₂CH₂NMe₂, 2-(PhO)C₆H₄, 2-CH₂C₅H₃N, 8-C₉H₆N (quinoline) and 2-(PPh₂)C₆H₄] are accessed in good yields (>85%) via standard imine condensation reactions. Reaction of ligand with Me₃Al at room temperature affords the corresponding complexes [(3,5-But2-2-(O)C₆H₂CH:NL)AlMe₂]; in the case of L = 8-quinoline, the same reaction conducted in refluxing toluene affords binuclear {[3,5-But2-2-(O)C₆H₂CHMeN-8-C₉H₆N]AlMe}₂ (3) by Me migration from metal to ligand. Further reaction of the di-Me compounds with B(CF₃)₃ in CD₂Cl₂ or C₆D₆ affords the cationic systems [(3,5-But2-2-(O)C₆H₂CH:NL)AlMe]+ (4a-e). The crystal structures of these complexes were determined. In 2a and 2c the representation ligands bind to the metal center via all three heteroatoms, the Al having a trigonal bipyramidal geometry, coordination may occur via N and O

only, and the Al is tetrahedral in some complex has a dimeric structure with the ligand adopting both tridentate and binucleating roles; the Al centers are trigonal bipyramidal [19].

Mixed ligand Aluminium (III) complexes involving Schiff bases [20] $[AIL_2L']$ (L = deprotonated salicylaldehyde (sald), o-aminophenol (oapH) or anthranilic acid (anthH) or 1-nitroso-2-naphthol (1 N_2N), and L' = monodeprotonated salicylidene-o-aminophenol (saloapH) or salicylideneanthranilic acid (salanthH)] have been synthesized and characterized by elemental and spectral studies.

The bidentate ligand, $3,5\text{-tBu-2-(HO)}C_6H_2(CH:NBut)$ [sal(tBu)H], was prepared by the condensation of one equivalent of a bulky amine with 3,5-di-tert-butylsalicylaldehyde. When one equivalent of Sal(tBu)H is added to MR_3 (M = Al, Ga, In, R = Me, Et) or $AlMe_2Cl$, compounds are obtained which have the general formula: $[sal(tBu)MR_2]$ (with M/R combinations, Al/Me (1), Al/Et (3), Ga/Et (4) and In/Et (5) and Sal(tBu)AlMeCl (2). The compounds were characterized by melting point, elemental analyses, IR, ^1H NMR, and in the case of 2 and 3 by single-crystal x-ray analysis [21].

A potentially tridentate [22] ligand, $3,5\text{-tBu}_2\text{-2-HOC}_6H_2CH$: $NC_6H_4NH_2\text{-2}$ (phensal(tBu)H_3), was prepared by the condensation of 1 equivalent of phenylenediamine with 3,5-di-tert-butylsalicylaldehyde.

Fig. - 3 : Structure of Schiff base complex

[phensal(tBu)H₂]GaMe₂

When one equivalent of this ligand was added to AlMe₃, [[phensal(tBu)HAlMe]₂] results. In contrast, this reaction with GaMe₃ produces [phensal(tBu)H₂]GaMe₂. When 1 or 2 equivalent of phensal(tBu)H₃ is combined with Et₂AlCl, [phensal(tBu)H₂]2AlCl forms. However the same reaction with Me₂GaCl leads to [phensal(tBu)H₂]Ga(Me)Cl. A cationic complex, {[phensal(tBu)H₂]₂Al} +Cl, is formed when complexes are dissolved in MeOH. The MeOH apparently mediates the formation of the cation but does not coordinate the cationic metal. [phensal(tBu)H₂]₂Al}+GaCl₄ is formed. In a similar manner, {[phensal(tBu)H₂]₂Al}+Me₂AlCl₂ is formed by adding Me₂AlCl to 3. The compounds were characterized by m.p., elemental analyses, IR, ¹H and ²⁷Al NMR, and in some complexes were analysed by single-crystal x-ray analysis.

The coordination behaviour of Schiff base derivative of semicarbazide and thiosemicarbazide, I (X = O, S), having the donor

groups NO or NS towards Al(III) was studied. The unimoleculerar, bimoleculerar and trimoleculerar reactions of aluminum isopropoxide with monobasic bidentate ligands gave colored solids [Al(OPr^i)$_2$(L)], [Al(OPr^i)(L)$_2$], and [Al(L)$_3$] where L = I, which were characterized by elemental analysis, molecular weight determination and molar conductance measurements. The UV, IR and NMR spectral studies indicate pentacoordinated and hexacoordinated geometries for the resulting complexes. Both the ligands and their complexes were screened for their fungicidal and bactericidal activities [23].
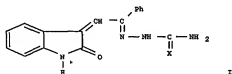
Fig.4- : Structure of Schiff base derived from Semicarbazide and Isatin

Readily accessible, chiral complexes of Al are effective and enantioselective catalysts for the phospho-aldol reaction under aerobic conditions. Chiral Al methyl/chloro complexes with bis(salicylidene)-trans-1,2-cyclohexanediamine derivative were prepared and crystal structures were studied for several of them. The (MeO)$_2$P(O)H adds to benzaldehydes in presence of AlXL (H$_2$L=bis(salicylidene)-1,2-trans-cyclohexanediamine, X=Me, Cl; H$_2$L=bis(3,5-di-tert-butylsalicylidene)-1,2-trans-cyclohexanediamine, X=Me to give (R)-(MeO)$_2$P(O)CHR(OH)

(R=H, 4-Br, 4-Me, 4-MeO, 4-NO$_2$, 4-ClC$_6$H$_4$CHO, 2-Cl, 2-Me and 2-MeOC$_6$H$_4$CHO) [24].

The effects of Schiff base-metallocomplexes on the corrosion of mild steel were investigated by corrosion weight loss measurements and surface analyses in various aqueous solution such as hydrochloric acid solution and pseudo cooling water. The maximum value of inhibition efficiency on the corrosion of mild steel in 1 moleculer/dm^3 hydrochloric acid solution was about 95.8% in the case of Indium(III) {N,N-bis(salicylaldehyde)-1,12-diaminododecane} complex. The molecule of Schiff base-metallo-complexes adsorbed on the surfaces of mild steels to depress the corrosion [25].

Schiff bases obtained from p-nitro- or p-hydroxybenzaldehyde and p- or o-phenylenediamine form adducts with anhydrous AlCl$_3$ or HgCl$_2$. The compounds were obtained by mixing C$_6$H$_6$ solution of the base with solution of the appropriate metal salt in the same solvent. The constitution of the compounds (AlCl$_3$)$_2$L, (AlCl$_3$)$_3$L, HgCl$_2$L$_2$, and HgCl$_2$L (L = Schiff base) was discussed on the basis of their ir spectra [26].

Complexes of Cr(III), Mn(III), Fe(III) and Al(III) with Schiff bases derived from the 2:1 condensation of 2-hydroxy-5-methylacetophenone and 2-hydroxy-5-chloroacetophenone with p-phenylenediamine (H$_2$L$_1$/H$_2$L$_2$) were prepared The antibacterial activities of the ligands and their complexes were evaluated. The

kinetic parameters of decomposition also were evaluated by both Freeman-Carroll and Sharp-Wentworth methods [27].
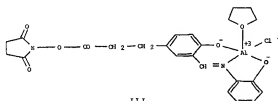
Fig. - 5 : Structure of Schiff base complex of Aluminium (III)

The complexes [28], LAlOSiPh3 [L=Salen(tBu) (N,N'-ethylenebis(3,5-di-tert-butylsalicylideneimine)) (11); Salpen(tBu) (N,N'-bis(3,5-di-tert-butylsalicylidene)-1,3-propanediamine) (12); Salophen(tBu) (N,N'-o-phenylenebis(3,5-di-tert-butylsalicylideneimine) (13); and Salomphen(tBu) (N,N'-(4,5-dimethyl-1,2-phenylene)bis (3,5-di-tert-butylsalicylideneimine)) (14)] have been formed by combining the five-coordinate aluminium alkyl starting materials L(tBu)AlR. All of the compounds were characterized spectroscopically and, in the some cases by x-ray crystallography.

Five-coordinate Aluminum [29] complexes with salicylideneamine derivative ligands were prepared.

This includes the compounds [salen(tBu)]AlCl (salen(tBu) = N,N'-ethylenebis(3,5-di-tert-butylsalicylideneamine) (1; salen), (N,N'-propylenebis(3,5-di-tert-butylsalicylideneamine) (2; salpen), (N,N'-phenylenebis(3,5-di-tert-butylsalicylideneamine) (3;salophen) and (N,N'-

(3,4-dimethylphenylene) bis(3,5-di-tert-butylsalicylideneamine))
(4; Salomphen) and the five-coordinate monomeric amides LAlNRR'
(L=Acen (N,N'-ethylenebis(3,5-di-tert-butyl(methyl) salicylideneamine); R, R' =
H, Ph ; R = R' = SiMe$_3$ and L = salen (R, R' = H, tBu, H, Ph , and H,
Dipp (2,6-diisopropylphenyl) ; R = R' = Me, Et, and SiMe3).
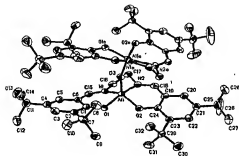
Fig. - 6 : Structure of Schiff base monomeric hydroxy complex
salen(tBu)AlOH

Additional the monomeric hydroxy complex salen(tBu)AlOH and its
condensation product, (salen(tBu)Al)$_2$O will be described. All of the
compounds were characterized by spectroscopic (^{1}H, ^{13}C, and ^{27}Al
NMR, IR) and physicochemical techniques. X-ray crystallographic data
are presented for 14 in monoclinic space group.

Proton-ligand and metal [Al(III), In(III), Ga(III)]-ligand
formation constants were detected pH-metrically at 35 and ionic strength
0.1 M (NaClO4) in aq. EtOH. The ligands are Schiff bases formed from
8-formyl-7-hydroxy-4-methyl-2H-1-benzopyran-2-one with aniline,
p-methylaniline and p-chloromethylaniline [30].

The Complexing of 13 Schiff bases [31] (formed by anilines and benzaldehydes) with AlCl$_3$ was studied spectrophotometrically in EtOH. Stability constants for 1:1 complexes are increase as electron donating power of substituents on the aniline portion of the Schiff base increase. Substituents on the benzal portion of the ligand enhance stability to a lesser extent. Electron withdrawing substituents reduce stability.

Aluminum, Gallium and Indium complexes [32] of sulfur containing Schiff bases M$_2$L$_3$ (M = Al, Ga, In; H2L$_2$-HOC$_6$H$_4$CH:NCH$_2$CH$_2$SH) and M(OR)L (R = iso-Pr, tert-Bu) were prepared The complexes were characterized by IR and NMR spectra.

Aluminum(III) complexes with hydrazide [33] Schiff bases of the type Al(HL)$_2$Cl and AlLCl (H$_2$L = hydrazide Schiff bases such as N-(salicylaldimino)acetamide, -benzamide, -salicylamide, -anthranylimide or disalicylaldiminooxamide, -malonamide and -succinamide) were prepared and characterized from elemental analysis and electronic and IR spectra. The complexes are highly insoluble in organic solvents and decomposed at >300 without melting. The ligands mostly chelate through the OH and C=N groups of the salicylaldimine moiety.

Reactions in 1:1:1 stoichiometry of Al(OPr-iso), with hexylene glycol (C$_6$H1$_4$O$_2$) and the Schiff base (SBH) resulted in the prepration of (SB)Al(C$_6$H1$_2$O$_2$) type of asymmetric derivative (SBH =

monofunctional bidentate Schiff base). Similar reactions in 2:1:2 moleculerar ratios yielded (S'B')Al(C$_6$H$_1$$_2O_2$)Al(S'B'), and S"B")Al(C$_6H_1$$_2O_2$)Al(S"B") type of complexes (S'B'H$_2$ and S"B"H$_2$ bifunctional tridentate and bifunctional tetradentate Schiff bases, representation). Suitable structures based on IR and NMR spectral studies are indicated for the resulting derivatives [34].

Stability constants of In(III), Al(III), Cu(II), Ni(II), and Hg(II) complexes with a Schiff base from vanillin and Tris buffer are reported at 35°C in aqueous medium. The trend of the stability of the present transition and nontransition metal complexes is discussed, and ascribed to the structure of the ligand and position charge and the electronegativity of the central metal ion [35].

The magnetic susceptibilities of Al Schiff base complexes, e.g. Al$_2$(o-OC$_6$H$_4$CMe:NCH$_2$CHMeO)$_3$, and Si Schiff base complexes, representation, indicating their diamagnetic character [36].

Schiff bases o-HOC$_6$H$_4$CMe:NR (LH; R=Bu, Ph) and o-HOC$_6$H$_4$CMe:N(CH$_2$)nN: CMeC$_6$H$_4$OH-o (L$_1$H$_2$; n=2, 3) reacted almost in millimolar ratio with Al(OCHMe$_2$)$_3$ in anhydrous benzene to give Al(OCHMe$_2$)3-nLn (n=1, 2, 3), Al(OCHMe$_2$)L1, and Al$_2$L1$_3$. The complexes were characterized by elemental analysis, molecular weight determination and ir spectra [37].

Al(OPr-iso)$_3$ reacted with the Schiff bases (I) (HL; R = Et, Pr, iso-Pr, Bu, iso-Bu, sec-Bu, Me$_3$C, Ph) in different stoichiometric

ratios to give dimeric $[Al(OPr-iso)_2L]_2$, monomeric AlL_3, and $Al(OPr-iso)L_2$ of moleculer association. The structure of the complexes was discussed from the IR data [38].

$(Me_2CHO)_3Al$ reacted with the bifunctional tridentate Schiff bases o-HOC$_6$H$_4$CMe: NCRR1CHR$_2$OH (H_2L; R, R1, R$_2$ = H; R, R$_1$ = H, R$_2$ = Me; R, R$_1$ = Me, R$_2$ = H; R, R$_2$ = H, R$_1$ = Et) in 1:1 and 2:3 moleculerar ratio to give $LAl(OCHMe_2)_2AlL$ and Al_2L_3, representation, in almost quantitativly yield. The complexes were characterized by their molecular weight (ebullioscopic determination) and ir spectra [39].

The Fe(III), Cr(III) and Al(III) complexes I (R = H, Me, CH$_2$OH, X = Cl or NO$_3$) of Schiff base ligands derived from ninhydrin with some amino acids (glycine, α-alanine, serine) were prepared and characterized by elemental analyses, IR, electronic spectra as well as conductance and magnetic measurements. Modes of bonding and geometrical structures for these chelates are proposed [40].
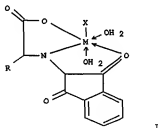
Fig. - 7 : Structure of **Schiff base complexes** derived from **ninhydrin and Amino Acid**

Complexes of AlCl$_3$ with benzaldehyde anil, tolualdehyde anil, p-dimethylaminobenzaldehyde anil and p-nitro benzaldehyde anil were obtained and characterised by their ir spectral studies. The ratio AlCl$_3$:anil is 1:1. The complexes are yellow and fairly stable in dry air, but moisture decomposed them. When heated they decomposed without exhibiting a well-defined m.p. [41].

The prepared in situ methyl(chloro)aluminum complex (2) from Me$_2$AlCl and the pendant arm tridentate Schiff base (schNMe$_2$H) was used to generate the methylaluminum cationic species [(schNMe$_2$)AlMe]+ in further reaction wth 1 equivalent `of AlCl$_3$ or NaBPh$_4$ as the chloride abstracting reagents. The exposure of the resulting methylaluminum cationic species to an excess of dry dioxygen at 0 degrees C afforded the alkoxyaluminum cationic species [(SchNMe$_2$)AlOMe]+ or [(SchNMe$_2$)AlOPh]+. The alkoxyaluminum cations proved to be a very efficient catalyst in the polymerization of epsilon-caprolactone [42].

Fig. - 8 : **Structure of Schiff base alkoxyaluminium cationic species, [(SchNMe$_2$)AlOMe]+**

The equimoleculerar reactions of Ph_3Bi with benzothiazoline ligands proceed with rearrangement of the benzothiazoline ring and give diphenylbismuth(III) derivative of Schiff bases, $Ph_2Bi[SC_6H_4N:C(R)CH_2C(O)R']$ (R $\doteq$ Me, CF_3; R' = Me, Ph, 2-thienyl). The modes of bonding and the probable structure of these synthesized derivative have been discussed on the basis of physicochemical and spectroscopic [IR, NMR (^{1}H and ^{13}C)] studies [43].

The equimoleculerar [44] reactions of Ph_3Bi with bifunctional tetradentate Schiff bases proceed with cleavage of two Bi-C bonds of Ph_3Bi and result in the formation of phenylbismuth(III) derivative $PhBi[RC(NC_6H_4S) CH_2(NC_6H_4S) CCOOCH_3]$ (R = C_6H_5, 4-ClC_6H_4, 4-BrC_6H_4, 4-C$H_3C_6H_4$). Physico-chemical, IR, and NMR (^{1}H and ^{13}C) spectral studies have been carried out to investigate the structural aspect of these derivatives, which reveal a pentacoordination around the central Bi atom.

The reactions of Schiff base ligands, prepared by the condensation of o-aminothiophenol with heterocyclic aldehydes like furfuraldehyde, thiophene-2-aldehyde, pyridine-2-aldehyde and indole-3-carbaldehyde were studied with $SbCl_3$ and $BiCl_3$. The complexes formed are $SbCl_3L$ and $BiCl_3L$ (L = RCH:NC_6H_4SH-2, R = C_4H_3O, C_4H_3S, C_5H_4N, C_8H_6N). These complexes were characterized from elemental analyses, moleculer weight determination, IR, NMR (^{1}H and ^{13}C) and x-ray diffraction data [45].

Aluminium compounds with organic ligands are widely used as reagents in organic synthesis. A class of air-stable, cationic, six-coordinate aluminium complexes of general formula [(Schiff base) Al(solv)$_2$]X has been introduced, and their utility as catalysts for the polymerization of propylene oxide has been demonstrated. Detailed preparation of representative members of this class based on salen (N,N'-bis (2-hydroxybenzylidene) ethylenediamine) and related ligands are presented [46].

The reactions of bimetallic-μ-oxoisopropoxide [MgO$_2$Al$_2$(OPri)$_4$] with Schiff bases (HLL') viz. salicylideneaniline (salanH), salicylidene-o-toluidine (saltolnH) or salicylidene-p-chloroaniline (salcanH) in the molar ratios 1:1, 1:2 and 1:3 yields [MgO$_2$Al$_2$(OPr^i)$_3$(LL')], [MgO$_2$Al$_2$ (OPr^i)$_2$(LL')$_2$] and [MgO$_2$Al$_2$(OPr^i)(LL')$_3$] (LL' = deprotonated Schiff base) respetively. The Schiff base derivatives of bimetallic [Mg(II), Al(III)]-μ-oxoisopropoxide were characterized by elemental analysis, molecular weight measurements, and spectral studies (IR, ^{1}H NMR ^{27}Al NMR). A dimeric structure for 1:1 and 1:2 and a monomeric structure for 1:3 Schiff base derivatives of bimetallic[Mg(II),Al(III)]-μ-oxoisopropoxide were tentatively proposed [47].

Some compounds of aluminium [48] having the general formula Al[SC$_6$H$_4$N:C(R) CH$_2$ C(O)R']$_3$ where R = CH$_3$, R' = CH$_3$ (1); R = CH$_3$, R' = C$_6$H$_5$ (2); R = CF$_3$, R' = $-C = CH - CH = CH$ (3);

R = CF$_3$, R' = C$_6$H$_5$ (4) have been synthesized by the reactions of Al(OPr^i)$_3$ and the corresponding ligands in 1: 3 molar ratios in benzene. Elemental and spectroscopic (IR, ^{1}H, ^{13}C, and ^{27}Al NMR) characterization of these monomeric compounds reveals monofunctional bidentate behavior of ligand moiety and the octahedral geometry around aluminum atom. Compound Al[SC$_6$H$_4$N:C(CH$_3$)CH$_2$COCH$_3$]$_3$ has been tested for its antifertility activity in male albino rats.

A wide range of bimetallic Al complexes are formed in combinations between Salen Schiff base ligands and either AlR$_3$ or AlR$_2$Cl. They are L(AlR$_2$)$_2$ and L(AlRCl)$_2$ with R = alkyl and L = salen(tBu) ligand with relatively unusual backbone connections between the N atoms, 1,2-cyclohexylene (salcen(tBu)), 1,4-butylene (salben(tBu)), 1,5-pentylene (salpten(tBu)), 1,6-hexylene (salhen(tBu)), and 1,4-phenylene (1,4-salophen(tBu)). The, previously unknown ligands
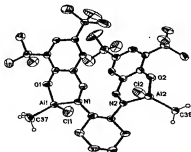
Fig. -9: ORTEP- View of schiff base aluminium complex [Salcen (tbu)Al (Me Cl$_2$)]

were employed with the backbones 1,4-bis(p-aminobenzyl)benzene (salmaben(tBu)), 1-(m-aminobenzoyl)-4-(m-aminobenzyl)benzene (salmabmaben(tBu)), and 4,4'-bis(m-aminobenzoyl)diphenylmethane (salmadmen(tBu)). The ligands for these compounds were designed to feature two group 13 sites at long and varying distances from one another. The compounds were characterized by elemental analyses, IR, ^{1}H NMR, and x-ray crystallography [49].

The ligands (RsalH2)$_3$tachH$_3$ (R=H, NO$_2$, OMe) were synthesized by Schiff base condensation between cis-1,3,5-triaminocyclohexane and a substituted salicylaldehyde, followed by reduction with KBH$_4$. Reaction of these compounds with Al(III) salts gives uncharged hexacoordinate N$_3$O$_3$ complexes Al(RsalH$_2$)$_3$tach. The complexes were characterized by a combination of IR, ^{1}H and NMR, and mass spectroscopy. Structures of Al(salH$_2$)$_3$tach and Al(NO$_2$salH$_2$)$_3$tach were detected by x-ray crystallography
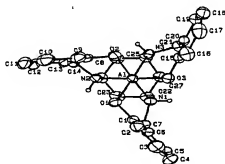
Fig. -10: ORTEP- Structure of [Al(salH$_2$)$_3$]

Some Schiff base derivatives of Al, $(Me_2CHO)_3$-$nAl[O(NH_2)C:NN:CMeR]n$ (n = 1, 2 and 3; R = 2-furyl, 2-thienyl, 2-pyridyl, 2-naphthyl) were synthesized by the reactions of semicarbazones of the Me ketones of heterocyclic aromatic compounds with Al isopropoxide in stoichiometric ratios in refluxing benzene. The replacement reactions of isopropoxy Al(III) derivatives with tert-BuOH also were studied. All these derivatives were characterized by conductance measurements, elemental analysis and molecular weight determination. Their probable structures were proposed from IR and ^1H NMR spectral studies [51].

Potentiometric equililbrium studies of Zn(II), Al(III), and Ga(III) complexes of Schiff bases (SB) of 3-amino-3-phosphonopropionic acid (3APP) and 5'-deoxypyridoxal (DPL) are described. Schiff base formation by 3APP and DPL was investigated by measurement of ^{31}P NMR spectra the mono-, di-, tri-, and tetraprotonated species, representation ^{31}P NMR spectroscopy was also useful in helping to assign the protonation sites on the Schiff base [52].

The reactions of $[Al(OPr\text{-}iso)_3]$ with I (R = H, R' = C_6H=OH or $C_{10}H_6OH$; R = Me, R' = C_6H_4OH), II, and III (R = H, Me, Ph) in 1:1 and 2:3 ratios gave $[Al(OPr\text{-}iso)L]$ and $[Al_2L_3]$, representation, in which L is the anion of the Schiff base (H_2L) formed by ring opening of (I), (II), and (III); e.g., o-HSC_6H_4N:CRR' formed from (I). The

Al(OPr-iso)L complexes undergo substitution reactions with tert-BuOH to give Al(OBu-tert)L. The complexes were characterized by elemental analysis and IR, UV, and NMR spectra and structures are proposed [53].
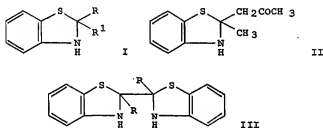
Fig. - 11 : Structure of the Schiff base species

PMR spectra of the Schiff bases, 2-hydroxy-1-naphthylidene-n-propylamine (I) and 2-hydroxy-1-naphthylidene-n-butylamine (II) and their Al(III) complexes obtained in reactions with aluminum isopropoxide, were recorded and discussed. The peaks of CH(azomethine proton) are given. Sharp singlets appear at 1.30 and 1.25 τ in (I) and (II), representation. For the aluminium complexes, this singlet is shifted considerably downfield, which may be due to the considerable deshielding of the proton caused by the coordination of N to the aluminium atom [54].

SbX$_3$/SbCl$_5$-L (1:1) complexes (X=Cl, Br; L=benzaldehyde/acetophenone S-benzyldithiocarbazate Schiff bases). were prepared and characterized by elemental analyses and spectral studies [55].

Triorganoantimony(V) Schiff base complexes R_3SbL, where R=Ph, p-tolyl or Me and H_2L are potentially tetradentate Schiff base ligands with ONNO donors, were synthesized and characterized. The Schiff bases were obtained by the condensation of ethylenediamine with acetylacetone (AcacenH$_2$) or with o-hydroxyacetophenone (ohacenH$_2$); propylenediamine with salicylaldehyde (SaltmH$_2$) or with o-hydroxyacetophenone (ohactmH$_2$) and o-aminophenol with glyoxal (GbapH$_2$). Moleculer weight determied in benzene reveals the monomeric nature of these complexes. IR and NMR data suggest seven coordinated Sb in these complexes [56].

The reactions of Schiff base ligands, prepared by the condensation of o-aminothiophenol with heterocyclic aldehydes like furfuraldehyde; thiophene-2-aldehyde, pyridine-2-aldehyde and indole-3-carbaldehyde were studied with SbCl$_3$ and BiCl$_3$. The complexes formed are SbCl$_3$L and BiCl$_3$L (L=RCH:NC$_6$H$_4$SH$_2$, R=C$_4$H$_3$O, C$_4$H$_3$S, C$_5$H$_4$N, C$_8$H$_6$N). These complexes were characterized from elemental analyses, molecular weight determination, IR, NMR (^{1}H and ^{13}C) and x-ray diffraction data [57].

S-Benzyl dithiocarbazate Schiff base complexes [58] of diphenylantimony(III) having the general formula Ph$_2$Sb[XC$_6$H$_4$CR: NNCS$_2$CH$_2$C$_6$H$_5$], (where R = H, X = o-OH; R = CH$_3$, X = p-F, p-Br, p-Cl, p-OH, p-OCH$_3$) have been synthesized by the reactions of Ph$_2$SbCl with the sodium salt of the corresponding ligands. These

derivatives have been characterized by elemental analyses and molecular weight measurements.

Monomeric complexes R_2SbXL [R=Ph, tolyl, Me]; H_2L are potentially tetradentate Schiff base ligands with ONNO donors, i.e., N,N'-bis(salicylidene) propylenediamine and -phenylenediamine] were synthesized; IR and NMR data suggest 7-coordinate Sb [59].

Several substituted tertiary aryl antimony(V) complexes of Schiff bases having the formula, R_3SbL [R = p-FC_6H_4, p-ClC_6H_4, C_6F_5, p-$CH_3C_6H_4$; L=N,N' - bis(salicylaldehyde)-o-phenylenediamine,2-HOC_6H_4CH: $NCH_2 CH_2N$:$CHC_6H_4OH_2$] were prepared by the reaction of R_3SbCl_2 with the sodium salt of the ligand, directly with the ligand in the presence of Et_3N, or by the reaction of $R_3Sb(OMe)_2$ with the ligand. A pentagonal bipyramidal structure having seven coordination around Sb has been suggested for these complexes [60].

ArRC:NR1 (L; R=H, Ar=1-naphthyl, Ph, R_1=CMe$_3$; R= 2-ClC$_6$H$_4$, R_1=CHMe$_2$, or R=Me, R_1=CMe$_3$, Ar=2-thienyl) reacted with HgCl$_2$, SbCl$_3$ and RhCl$_3$ to give HgCl$_2$L$_2$, SbCl$_2$L$_2$.MeOH and RhCl$_3$L$_3$, representation Spectroscopic evidence by IR, ^{1}H, ^{13}C, ^{199}Hg NMR, mass spectroscopy as well as elemental analysis showed weak dative bond between these imines and the metals. These complexes were neutral as indicated by their electric conductance [61].

Monomeric R_3SbBrL (R=Me or Ph; HL=N-(salicylidene)-o-phenylenediamine (spdH), N-(2-hydroxy-1-naphthalidene)-o-phenylenediamine (npdH), N-salicylidene-2-aminopyridine (sapH), and N-(2-hydroxy-

1-naphthalidene)-2-aminopyridine (napH) were prepared and characterized. IR and NMR data suggest 7-coordinated structure for $R_3SbBr(spd)$ and $R_3SbBr(npd)$, indicating the tridentate nature of spdH and npdH. $R_3SbBr(sap)$ and $R_3SbBr(nap)$ are 6-coordinated indicating the bidentate nature of sapH and napH [62].

Transition metal, rare earth metal and main group metal complexes with the Schiff bases salicylidene-2-aminophenol, salicylidene-2-hydroxy-1-naphthylamine, 2-hydroxy-1-naphthylmethylidene-2'-aminophenol, and 2-hydroxy-1-naphthylmethylidene-2'-hydroxy-1'-naphthylamine were prepared and characterized by IR spectra. The Schiff bases are tridentate and form monoanionic and dianionic complexes with coordination nos. of 4 and 6 [63].

Complexes of some Schiff bases [64] with antimony(V), $[SbCl_2L_2]Cl$ (HL=R-o-HOC$_6$H$_3$CH:NC$_6$H$_4$OH-o' (R=H, 5-Cl), 3,4,5-Me$_3$-o-HOC$_6$HCH:NC$_6$H$_4$OH-o') were prepared and characterized by elemental analysis, molecular weight, molecular conductance, and spectral (IR,^{1}H NMR) methods. L' coordinate via N and deprotonated O of the R-substituted aromatic ring.

Hexacoordinated complexes [65] of antimony(V). trans-$[SbCl_4L_2]Cl$ (L=Schiff base derived from salicylaldehyde or its deriv. and amine) and cis-$[SbCl_4L_1]Cl$ (L$_1$=Schiff base derived from salicylaldehyde or its derivative. and diamine) were prepared. The complexes were characterized by elemental analyses, molecular

weight determination., conductance measurements and spectral results. Coordination of L or L_1 may be through azomethine Nitrogen the hydroxyl group does not participate.

A series of Schiff base complexes of organoantimony(V) having formula R_3SbL (R=Ph or Me, L=dibasic tetradentate ligands with the ONNO donor system) have been synthesized. The complexes are yellow to orange in colour. These complexes have been characterized by elemental analysis and i.r. and p.m.r. spectral data. Based on these measurements a pentagonal bipyramidal structure has been proposed for each one of these complexes [66].

SbX_2L (X = Br, Cl; HL = $RR_1C:NNHC(S)SMe$ (R = R_1 = Me, Ph; R = Me, R1 = Et, Ph) and $SbCl_4L$ were prepared and characterized by IR spectra and electric conductance measurements. SbX_2L are stable in air, melt without decomposition, and are monomeric and nonelectrolytes. The ligands are bidentate with coordination through the S and N atoms [67].

Monomeric triorganoantimony(V) complexes R_3SbL [R=Me, Ph; LH_2=tridentate Schiff bases, $HOC_6H_4CR_1:NXOH$ (R_1=H, Me; X=$(CH_2)n$, n=2, 3, CH_2CHMe)] were synthesized and an octahedral coordination environment for Sb was suggested on the basis of spectral (IR, UV) data [68].

Six-coordinate $[SbL_2Cl_2]Cl$ (HL = 2-R-4-R_1-5-$R_2C_6H_2N$: C(Me)CH: C(OH)CH$_3$, R=Cl, Me, OMe, R_1=R_2=H; R=R_2=H, R_1=Cl,

Me, OMe; $R = R_2 = OEt$, OMe, $R_1 = H$) were prepared from $SbCl_5$ and HL in dry C_6H_6. $[SbL_2Cl_2]Cl$ were characterized by IR and electronic spectra and electric conductance The Ligand is bidentate with coordination through N and the deprotonated OH [69].

The complexes RCl_2SbL [R = Ph, Cl, L = I (Z = O); R = Ph, L = I (Z = S)] were prepared by treatment of $[NH_4][PhSbCl_5]$ or $SbCl_5$ with the appropriate dimethyltin-I complex and characterized by spectral methods. These complexes have an octahedral configuration with meridional ONO [70].

FSb(sab), ClSb(sab) $[SabH=2-HOC_6H_4CH:NC_6H_4OH_2]$, and ClSb(sat) $[SatH=2-HOC_6H_4CH:NC_6H_4SH_2]$ were prepared and characterized by[121]Sb Moessbauer, IR, and mass spectra. The occurrence of chelation by the tridentate ligand is inferred from the IR data. The magnitudes suggest a consistent p-character of the Sb lone-pair orbital [71].
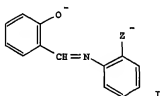
Fig. – 12 : Structure of Schiff base

The title compounds were prepared by the reactions H_2L + 2

NaOMe → Na_2L + 2 MeOH; Na_2L + R_2SnCl_2 → R_2SrL + 2 NaCl (H_2L=I; Y=H or Me; R = Ph, Bu, CH_2 Ph, p-tolyl, or ClC_6H_4). A second series of compounds was prepared by the reactions Ph_3SnCl + NaOMe → $Ph_3Sn(OMe)$+ NaCl; $Ph_3Sn(OMe)$ + HL → Ph_3SnL + MeOH [HL = $RS(HS)NN:CR_1R_2$; R =Me or CH_2Ph; R_1=H or Me; R_2=Me, Et, or 2-pyridiyl]. A third series was prepared by the reaction HL + SbCln → HL.SbCln (HL = II; n = 3 or 5; X=H, m-NO_2, p-Me, p-OM, or p-NO_2). The bactericidal activity of the compounds was screened against Bacillus subtilis, B. pumilus, and Staphylococcus aureus, the fungicidal activity against ·Fusarium moniliforme, Helminthosporium, and Aspergillus terrus, and the insecticidal activity against the cockroach (Periplaneta americana). Structure-activity relations were established. Compounds of the 3rd series showed the highest bactericidal activity, against S. aureus and B. subtilis [72].
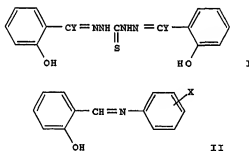
Fig. - 13 : Structure of Schiff base

The preparation. of FSb(sab), ClSb(sab), and ClSb(sat) is reported, where sab$_2$- and sat$_2$- are Schiff base chelating ligands I (X=O, S) having the donor systems ONO and ONS, representation These Sb(III) complexes were characterized in the solid state by mass, IR and[121]Sb Moessbauer spectroscopic techniques [73].
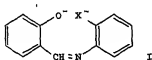
Fig. - 14 : Structure of Schiff base

The complexes Ph$_3$SbCl(OC$_6$H$_4$CR:NR$_1$-o) (R=H, R$_1$=Me, Et, Pr, Bu, Ph, p-MeC$_6$H$_4$, R=Me, R$_1$ = Me, Bu, Me$_2$CHCH$_2$) were prepared in 35-72% yields by treating Ph$_3$SbCl$_2$ with NaOC$_6$H$_4$CR:NR$_1$-o. Ph$_3$Sb(OMe)OC$_6$H$_4$CR:NR$_1$-o (R=H,R$_1$=Me; R=R$_1$=Me) were similarly prepared from Ph$_3$Sb(OMe)$_2$ and HOC$_6$H$_4$CR:NR$_1$ [74].

The direct interactions of SbCl$_3$ and SbCl$_5$ with salicylideneaniline and its amine ring-substitutes derivative result in the formation of adducts with 1:1 stoichiometry. The synthesized compounds were characterized through elemental analysis conductance measurements, and IR data. The ligands coordinate to the metal atom through their azomethine nitrogen atoms to give four- and six-coordinate Sb complexes [75].

The complexation reactions between Sb(III) and Schiff bases derived from salicylaldehyde and glycine salicylaldehyde and glutamic acid were synthesized [76].

The reactions of $Sb(OPr-iso)_3$ in 1:1, 1:2, and 1:3 moleculerar ratios with the Schiff bases $o-HOC_6H_4CMe:NR$ (HL; R=Pr, Bu, Ph) gave the monomeric complexes $[Sb(OPr-iso)_2L]$, $[Sb(OPr-iso)L_2]$, and $[SbL_3]$, representation The structures of the compounds are discussed on the basis of IR spectra [77].

A polarographic study of the complexes of Sb(III) with Schiff bases derived from salicylaldehyde, vanillin and Tris buffer was carried out in acetate buffer at 3 different temperatrue. The metal ion undergoes a quasireversible reduction, while the complex is reduced irreversibly at the cropping Hg electrode. The overall forward electrode reaction rate constant (kf0)B is calculated by applying 3 different treatments [78]. ,

Several Schiff base complexes of Sb(III) were prepared by the reaction of $[Sb(OPr-iso)_3]$ with Schiff bases having the donor system, O-N-O. The reactions in 1:1 and 2:3 moleculerar ratios [Sb(OPr-iso)_3:Schiff base] yielded $[Sb(OPr-iso)(SB)]$ and $]Sb_2(SB)_3]$ types of derivative $(SBH_2=$o-hydroxyacetophenone-2-hydroxy-1-propylimine,o-hydroxyacetophenone-3-hydroxy-1-propylimine, salicylidene-2-hydroxyethylamine, salicylidene-2-hydroxy-1-propylamine, and 2-hydroxy-1-naphthylmethylene-2-hydroxyethylamine). In the resulting Schiff base complexes the central Sb atom is tetracoordinated, as indicated by the monomeric state determined ebullioscopically. The IR spectra of the resulting complexes were recorded and tentative structures are proposed. The

thermogravimetric analysis of Sb[OPr-iso)(SB], where SBH = salicylidene-2-hydroxy-1-propylamine, was also carried out [79].

Schiff bases were prepared using Tris buffer with salicyladldehyde, vanillin, benzaldehyde, and their color, solubility. in aqueous and non-aqueous media, melting point, and stability were studied. Use of these solution as ligands in the polarographic of Sb and Bi in acetate solution resulted in single well defined reduction waves. A small prewave existed at low ligand concentration and at higher temperature in the case of Sb and is explained in terms of the characteristics of the complex. Formation of a complex species is indicated by a shift in the half-wave potential to more negative values [80].

The ^{121}Sb Moessbauer spectra at 9 and 78 K of Ph$_3$SbCl (oxin) (oxin = 8-hydroxyquinolinate) and Ph$_3$SbR [R=(R$_1$=H, Me)] were discussed; a mer-octahedral structure was proposed [81].
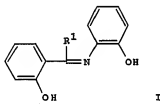
Fig. - 15 : Structure of Schiff base oxin

Reactions of [(iso-PrO)$_3$Sb] with bidentate Schiff bases (SBH), having the general formula o-HOC$_6$H$_4$CH:NR (R=Pr, Bu, Ph) in

different stoichiometric ratios gave [(iso-PrO)$_2$Sb(SB)$_2$] and [Sb(SB)$_3$] types of prouducts in which the central Sb atom appears to be tetra-, penta- and hexacoordinated, representation. The IR spectra of the resulting derivative were recorded and tentative assignments made [82].

The Schiff bases PhCH:NZOH (HL), where Z = (CH$_2$)$_2$, (CH$_2$)$_3$, and CH$_2$CHMe, were prepared and their reactions with [(iso-PrO)$_3$Sb] in moleculere ratios 1:1, 2:1, and 3:1 gave [(iso-PrO)$_2$SbL,] [(iso-PrO)SbL$_2$], and [SbL$_3$], representation, in which the coordination number are 4, 5, and 6, representation The compounds were characterized by chemical analysis and IR spectra [83].

The triorganoantimony (V) complexes [84] with tridentate ligands, containing ONO and ONS as donor atoms, were prepared. Ligands were obtained by condensation of salicylaldehyde with o-aminophenol (sabH), salicylaldehyde with o-aminothiophenol (satH), acetylacetone with o-aminophenol (aaH), and benzoylacetone with o-aminophenol (baH). Me$_2$Sb(sab), Ph$_3$Sb(sab), Ph$_3$Sb(sab), Ph$_3$Sb(baH), and Ph$_3$Sb(aaH) complexes were examined by PMR and UV spectroscopy.

Reactions of SbCl$_3$, SbBr$_3$, and SbCl$_5$ with the planar transition metal compounds, N,N'-ethylenebis(salicylideneiminato)metal(II), [M-(saen)], where M is Co(II), Ni(II), or Cu(II), leads to the formation of 1:1 adducts in which the planarity about the transition

metal ion is retained. To clarify the question of local symmetry about the acceptor metal in such adducts, substitution products of the form Ni(saen)·M'(CO)$_4$ (where M' = Mo, W), Ni(saen)-Mn(CO)$_3$X (X v Cl-, Br-), and Ni(aben)Mn(CO)$_3$X have been isolated [Ni(aben) = N,N'-ethylenebis(o-aminobenzylidene-iminato)nickel(II)]. The IR spectra of these compounds over the carbonyl region have been. used in assigning structures to these complexes [85].

The complexing of aromatic azo and azomethine compounds with SbCl$_3$ and BF$_3$ (the latter added as the etherate) were investigated by a spectrophotometric method (300-600 nm.) and cheraterized by i.r. , u.v. visible, n.m.r. spectral studies [86].

Triphenylantimony(V) isopropoxide, [Ph$_3$Sb(OPri)$_2$] reacts with monofunctional bidentate benzothiazoline ligands 2-R$_2$-R'C(O)CH$_2$benzothiazoline [R=CH$_3$, R'= CH$_3$ (1); R=CH$_3$, R'= C$_6$H$_5$ (2); R=CH$_3$, R' = 4-CH$_3$C$_6$H$_4$ (3); R=CH$_3$, R'=4-ClC$_6$H$_4$ (4); and R= CF$_3$, R'=C$_6$H$_5$ (5)] in 1:1 molecular ratio in refluxing benzene solution to give corresponding triphenylantimony(V) ·derivative, Ph$_3$Sb(OPri)[2-SC$_6$H$_4$NC(R)CH$_2$C(O)R']. These synthesized compounds were characterized by elemental analyses, moleculer weight measurements and IR as well as NMR (^{1}H and ^{13}C) spectral studies [87].

Antimony(III) di-phenyl and chloro-phenyl derivative of monofunctional tridentate ligands, having the general formula

PhXSb[SC$_6$H$_4$N:C(R)CH$_2$C(O)R'] [where X = Ph (1-4); Cl (5-8);
R=CH$_3$, R'=CH$_3$ (1,5); R=CH$_3$, R' = C$_6$H$_5$ (2,6); R=CF$_3$, R'= 2-C$_4$H$_3$S
(3,7); R=CF$_3$, R'=C$_6$H$_5$ (4,8)] have been synthesized by reaction of
Ph$_n$SbCl$_{3-n}$ (where n=1 and 2) and the corresponding sodium salt of
benzothiazoline ligands in 1:1 molecularar ratio in refluxing benzene.
Products have been characterized by elemental analysis, molecular
weight measurements and IR as well as NMR (^{1}H and ^{13}C) spectral
studies suggested a five coordination environment arround matal
atom [88].

Reactions of triphenylantimony(III) with the tetradentate Schiff
bases, aroylpyruvate bis(2-mercaptophenyl)imines in equimolecularar
ratios yield the phenylantimony(III) dithiolato derivative,
PhSb[RC[NC$_6$H$_4$S$_2$)CH$_2$(2-SC$_6$H$_4$N)CCO$_2$Me-S,S',N,N'] (R=C$_6$H$_5$, 4-
ClC$_6$H$_4$, 4-BrC$_6$H$_4$, and 4-MeC$_6$H$_4$). These derivative were characterized
by elemental analyses, moleculer weight measurements, and IR as
well as NMR (^{1}H and^{13}C) spectral studies, which reveal a five
coordination around the central antimony atom [89].

N-(salicylidene)-o-mercaptoaniline alkyldithiocarbonate derivative of
Sb(III) were synthesized by substitution reactions of chlorobis
[N-(salicylidene)-o-mercaptoaniline antimony(III), Sb[SC$_6$H$_4$N: CHC$_6$I$_4$OH]$_2$Cl,
dichloro [N-(salicylidene) -o-mercaptoaniline] antimony(III), Sb[SC$_6$H$_4$N:
CHC$_6$I$_4$O]Cl$_2$ and monochloro[N-(2-oxybenzylidene)-o-anilinethiolato]
antimony(III), Sb[SC$_6$H$_4$N: CHC$_6$H$_4$O]Cl with potassium alkyl

xanthates in benzene/CS_2 in 1:1, 1:2 and 1:1 moleculerar ratios, representation The yellow or orange crystal complexes were characterized by elemental analyses, melting point, molecular weight determination as well as IR and NMR (^{1}H and ^{13}C) spectroscopy [90].

Some arylantimony(V) triphenylgermylpropionates, $(Ph_3GeCHR_1$ $CHR_2CO_2)_nSbAr_{(5-n)}$ (R_1=H, Ph; R_2=H, Me$_3$; n=1, 2) were synthesized and characterized by elemental analysis, IR, ^{1}H-NMR, ^{13}C-NMR and mass spectroscopy. The crystal structures of $Ph_3GeCH(Ph)CH_2CO_2SbPh_4$ and $[Ph_3GeCH_2CH (CH_3)CO_2]_2Sb(4-ClC_6H_4)_3$ were detected by x-ray diffraction. The in vitro antitumour activities of some selected compounds against five cancer cells are reported [91].
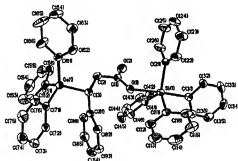
Fig. - 16 : **Crystal structure of $[Ph_3GeCH(Ph)CH_2CO_2]$ SbPh$_4$**

The Schiff base ligands were obtained by condensation of salicylaldehyde with amines (ethylamine, aniline, o-toluidine), amides (acetamide, benzamide) and ureas (urea, thiourea). In case of

antimony triiodide, two iodines are readily attacked, forming SbL_2I complexes (HL = Schiff base), but in case of antimony trichloride all the three chlorines are attacked, forming SbL_3 complexes. The complexes with urea and thiourea, SbLX (H_2L = Schiff base, X = Cl or I), have tetradentate Schiff base ligands [92].

Some pentacoordinated triaryl-As(V) complexes of Schiff bases Ar_3AsL (Ar = C_6H_5, p-$CH_3C_6H_4$, p-ClC_6H_4, p-FC_6H_4 and C_6F_5; L = dibasic tri- and tetradentate ligands with ONO and ONNO systems, i.e. salicylaldehyde condensation products with ethylenediamine, o-aminophenol and o-phenylenediamine) were synthesized along with some triarylantimony complexes with similar tridentate ligands. The complexes, which are yellow coloured solids, and characterized by elemental analyses, IR, ^1H and ^{19}F NMR spectral data. sp^3d and sp^3d^2 hybridization was suggested for the As and Sb derivatives from spectral data [93].

R_2SbXL, where R = Ph, p-tolyl or Me and H_2L are potentially tetradentate Schiff base ligands with ONNO donors, were synthesized and characterized. The Schiff bases obtained by the condensation of ethylenediamine with salicylaldehyde (salenH) and o-aminophenol with glyoxal (gbapH). Molecular weight-determination in benzene reveals the monomeric nature of these complexes. IR and NMR data suggest seven-coordinated Sb in these complexes [94].

The triorganoantimony(V) Schiff base [95] complexes R_3SbL, where R=Ph, p-tolyl or Me and H_2L are potentially tetradentate Schiff base ligands with ONNO donors, were synthesized and characterized. The Schiff bases were obtained by the condensation of ethylenediamine with acetylacetone (acacenH) or with o-hydroxyacetophenone (ohacenH); propylenediamine with salicylaldehyde (saltmH) or with o-hydroxyacetophenone (ohactmH) and o-aminophenol with glyoxal (gbapH). Moleculer weight determination in benzene reveals the monomeric nature of these complexes. IR and NMR data suggest seven coordinated Sb in these complexes.

The diphenylantimony(III) complexes having the general formula $Ph_2Sb[XC_6H_4CR:NNCS_2CH_2C_6H_5]$, (where R=H, X = o-OH; R = CH_3, X = p-F, p-Br, p-Cl, p-OH, p-OCH$_3$) have been synthesized by the reactions of Ph_2SbCl with the sodium salt of the corresponding ligands. These derivatives have been characterized by elemental analyses and molecular weight measurements. Plausible structures have been suggested on the basis of spectral evidences [96].

Monomeric complexes R_2SbXL [R = Ph, tolyl, Me; H_2L are potentially tetradentate Schiff base ligands with ONNO donors, i.e., N, N'-bis (salicylidene) propylenediamine and -phenylenediamine were synthesized; IR and NMR data suggest 7-coordinate Antimony [97].

Several substituted tertiary aryl antimony (V) complexes of Schiff bases having the formula, R_3SbL [R = p-FC_6H_4, p-ClC_6H_4, C_6F_5, p-CH$_3C_6H_4$; L=N,N'-bis(salicylaldehyde)-o-phenylenediamine, 2-HOC_6H_4CH:NCH$_2$CH$_2$N: CHC_6H_4OH$_2$] were prepared by the reaction of R_3SbCl_2 with the sodium salt of the ligand, directly with the ligand in the presence of Et$_3$N, or by the reaction of $R_3Sb(OMe)_2$ with the ligand. A pentagonal bipyramidal structure having seven coordination around Sb has been suggested for these complexes [98].

SbX_3 (X = Cl, Br) and $SbCl_5$ with Schiff bases from condensation of 2-aminothiazole or 2-aminobenzothiazole with salicylaldehyde or 2-hydroxy-1-naphthaldehyde gave 1:1 adducts. The compounds were characterized by conductance and thermal analysis and IR spectra. The ligands coordinate to the Sb atom through their azomethine N atom and not through phenolic O and S-atom of the ring [99].

Monomeric R_3SbBrL (R=Me or Ph; HL=N-(salicylidene)-o-phenylenediamine (spdH), N-(2-hydroxy-1-naphthalidene)-o-phenylenediamine (hnpdH), N-salicylidene-2-aminopyridine (sapH), and N-(2-hydroxy-1-naphthalidene)-2-aminopyridine (napH) were prepared and characterized. IR and NMR data suggest 7-coordinated structure for $R_3SbBr(spd)$ and $R_3SbBr(npd)$, indicating the tridentate nature of spdh and npdH. $R_3SbBr(sap)$ and $R_3SbBr(nap)$ are 6-coordinated indicating the bidentate nature of

sapH and napH [100].

Several Schiff base complexes of Sb (III) were prepared by the reaction of [Sb(OPr-iso)$_3$] with Schiff bases having the donor system, O-N-O. The reactions in 1:1 and 2:3 moleculerar ratios [Sb(OPr-iso)$_3$]:Schiff base yielded [Sb(OPr-iso)(SB)] and [Sb$_2$(SB)$_3$] types of derivative (SBH = o-hydroxyacetophenone-2-hydroxy-1-propylimine, o-hydroxyacetophenone-3-hydroxy-1-propylimine, salicylidene-2-hydroxyethylamine, salicylidene-2-hydroxy-1-propylamine, and 2-hydroxy-1-naphthylmethylene-2-hydroxyethylamine). In the resulting Schiff base complexes the central Sb atom is tetracoordinated, as indicated by the monomeric state detected ebullioscopically. The IR spectra of the resulting complexes were recorded and tentative structures are proposed. The thermogravimetric analysis of [Sb(OPr-iso)(SB)], where SBH = salicylidene-2-hydroxy-1-propylamine, was also carried out [101].

Complexes of monochlorodiorganoantimony (V) moieties with dianionic ONO tridentate ligands. Complexes I (R, R$_1$, R$_2$, R$_3$ given; Me, H, R$_2$R$_3$ = HC:CHCH:CH; Me, Me, H, Ph; Ph, H, R$_2$R$_3$ = HC:CHCH:CH; Ph, Me, H, Ph; Ph, Me, H, Me) were prepared by metathetic reactions of Me$_3$SbL with R$_2$SbCl$_3$ to give I and Me$_3$SbCl$_2$ or Me$_2$SnL with R$_2$SbCl$_3$ to give I and Me$_2$SnCl$_2$ [L=p--OC$_6$H$_4$CH:NC$_6$H$_4$O--o, PhC(O-):CHCMe:NC$_6$H$_4$O--o, MeC(O-):CHCMe:NC$_6$H$_4$O--o] [102].
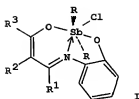
Fig. - 17 : Structure of Antimony (III) Complexes with dianionic ONO tridentate ligands

The reactions of bis(dialkyldithiocarbamato)arsenic(III) chloride with sodium salts of dialkyldithiophosphates in 1:1 moleculerar ratio give the corresponding mixed derivative of the type $[R_2NCS_2]_2AsS_2P(OR')_2$ [where, R = CH_3 and C_2H_5; R'=Et, Prn, Pri, Bun and Bui]. These derivatives are yellow coloured solids or yellow viscous liquids. All these synthesized derivatives are soluble in common organic solvents such as benzene, chloroform, carbondisulfide, acetone, and dichloromethane. These derivative have been characterized by melting point (only solid derivative), elemental analysis (C, H, N, S, and As) as well as spectral IR, NMR [^{1}H, ^{13}C, and ^{31}P] studies [103].

The dialkyldithiocarbamates complexes $[C_6H_3MeS_2MS_2CNR_2]$ (M=As and Bi; R = CH_3, C_2H_5 and CH_2-CH_2) were prepared by the reaction of toluene-3,4-dithiolatoarsenic(III) and -Bi(III) chlorides $[C_6H_3MeS_2MCl]$ (M=As and Bi) with Na/ammonium salts of

dialkyldithiocarbamates [XS_2CNR_2] ($X=Na$ and NH_4; $R=CH_3$, C_2H_5 and CH_2-CH_2). These derivatives were characterized by melting point, elemental analysis (C, H, N, S and As/Bi) and spectroscopic studies (IR, ^1H and ^{13}C NMR). Single crystal x-ray diffraction analyses of toluene-3,4-dithiolatoarsenic(III) dimethyldithiocarbamate and toluene-3, 4-dithiolatoarsenic(III) pyrrolidine-dithiocarbamate revealed a monodentate chelating mode of the di-Me as well as the pyrrolidine-dithiocarbamate moieties in these complexes [104].

The reactions of [R_2NCS_2]$_2$AsCl with KS_2COR' in 1:1 molecurlar ratio at room temperature readily gave mixed derivative [R_2NCS_2]$_2$AsS$_2COR'$ [where, $R = CH_3$ and C_2H_5; $R'=Et$, Pr, Pr^i, Bu and Bu^i]. These derivatives are yellow crystal solids. All these synthesized derivatives are soluble in common organic solvents (benzene, CHCl$_3$, CS$_2$, acetone and CH$_2$Cl$_2$, etc.). These derivatives were characterized by melting point elemental analysis (C, H, N, S and As) as well as spectral IR, NMR [^1H and ^{13}C] studies. From these studies tentative structures with distorted octahedral geometry for these derivative are proposed [105].

Some toluene-3,4-dithiolatoarsenic(III) alkyldithiocarbonate derivative [($MeC_6H_3S_2$)As(S_2COR)] [where, $R=Et$, Pr, i-Pr, Bu and i-Bu] were synthesized by the reactions of toluene-3,4-dithiolatoarsenic(III) chloride with potassium salts of

alkyldithiocarbonates in equimoleculerar ratios in anhydrous benzene and carbon disulfide (1:1) mixture at room temperature. All these derivatives are soluble in common organic solvents like benzene, carbon disulfide, chloroform, acetone and DMSO. These synthesized derivatives were characterized by elemental analysis (C,H, S and As), melting point as well as IR and NMR (^{1}H and ^{13}C) spectral studies [106].

Ethynylarsine is synthesized by reaction of arsenic trichloride with ethynyltributylstannane followed by a chemoselective reduction of the formed ethynyldichloroarsine. The base-induced rearrangement of compounds on a solid base in VGSR conditions leads to ethylidynearsine characterized by ^{1}H and ^{13}C NMR and by microwave spectroscopy. The rotational spectrum of complex is recorded in the frequency range 90-470 GHz. Rotational and centrifugal distortion constants are detected and the quadrupole hyperfine structure is analyzed [107].

Some monophenylarsenic(III) complexes of the type PhAs[RC(NC$_6$H$_4$S)CH$_2$ (NC$_6$H$_4$S)CR$_1$] (where R=CH$_3$, R$_1$=CH$_3$, C$_6$H$_5$ and 4-CH$_3$C$_6$H$_4$; R=CF$_3$, R$_1$ = CF$_3$ and C$_4$H$_3$S) were synthesized by the reactions of monophenylarsenic(III) chloride with the corresponding Schiff bases in equimoleculerar ratios in benzene. All these derivatives were characterized by the elemental analysis,

molecular weight measurements and the the the structure was proposed on the basis of IR and NMR (^{1}H, ^{13}C & ^{19}F) spectral studies [108].

The reactions between Bi Br$_3$ has afforded crystals of centrosymmtric, tetrameric complexes [Bi Br$_{12}$ (PEt$_3$)] in which Bermouth centre is octhadrally coordinatd and bonded to are phosphore ligand. An alternative structurala rrangement for moophosphore complex ha been found in a PMe$_3$ complex SbI$_3$ [{SbI$_3$(PMe$_3$)}]$_n$ which is polymeric although it bridges of two types between antimony centers like a dimer similarty structure oberved for the complexes [E$_2$Br$_6$(dmpe)] E=b or Bi dmpe = 1, 2 bis (dimethylphosphino) ethane] and the factor affectory which structural isomer is adopted i comparision with range of transfection metal complexes have been discued, an isomeric ttrameric form of [bBr$_3$(dmpe)] has been isolated all the complexes are caractrized 1H NMR, X-ray studies. Preparation and structural characterization [109] of triaryl metal(V) complexes (M=As, Sb) of tri- and tetradentate Schiff bases. Hitherto unreported pentacoordinated triaryl-As(V) complexes of Schiff bases Ar$_3$AsL (Ar=C$_6$H$_5$, p-CH$_3$C$_6$H$_4$, p-ClC$_6$H$_4$, p-FC$_6$H$_4$ and C$_6$F$_5$; L=dibasic tri- and tetradentate ligands with ONO and ONNO systems, i.e. salicylaldehyde condensation products with ethylenediamine, o-aminophenol and o-phenylenediamine) were

synthesized along with some triarylantimony complexes with similar tridentate ligands. The complexes, which are yellow crystal solids, were characterized by elemental analyses, IR, ^{1}H and ^{19}F NMR spectral data. sp^{3}d and sp^{3}d^2 hybridization was suggested for the As and Sb derivative, representation, from spectral data.

N,N'-Ethylenebis(salicylideneiminato)metal(II) complexes [M(salen)], where M is Co(II), Ni(II), or Cu(II), and also the Schiff base ligand, react with PCl$_3$ and AsCl$_3$ to yield cyclic derivative In the Schiff-base complexes the essentially square planar stereochemistry of the metal ion produces tetrahedral [Co(II), Cu(II)] or octahedral [Ni(II)] environments after reaction with PCl$_3$ or AsCl$_3$. These systems have been characterized by magnetic measurements, and UV and IR spectroscopy [110].

Me$_3$SiOAc or PhAsO$_3$H$_2$ on reaction with [Al(OPr-iso)$_3$] yields [Me$_3$SiOAl(OPr-iso)$_2$] and [PhAs(O)O$_2$Al(OPr-iso).] The isopropoxy groups in these derivatives further undergo facile reactions with bidentate Schiff bases, derived from salicylaldehyde or o-hydroxynaphthaldehyde and p-XC$_6$H$_4$NH$_2$ (X=F,Cl,Br,NO$_2$)] giving colored Me$_3$SiOAl(SB)$_2$ and PhAs(O)O$_2$Al(SB). The Si-Al type of compounds are monomeric nonelectrolytes in DMF and DMSO, where as the As-Al type of derivative are insoluble in most of the organic solvents and appear to be polymeric in nature [111].

Reactions of triphenylantimony (III) with the tetradentate Schiff bases, aroylpyruvate bis(2-mercaptophenyl)imines in equimoleculerar ratios yield the phenylantimony(III) dithiolato derivative, PhSb[RC(:NC$_6$H$_4$S$_2$) CH$_2$(2-SC$_6$H$_4$N:)CCO$_2$Me-S,S',N,N'] (R = C$_6$H$_5$, 4-ClC$_6$H$_4$, 4-BrC$_6$H$_4$, and 4-MeC$_6$H$_4$). These derivatives were characterized by elemental analyses, molecular weight measurements, and IR as well as NMR (^{1}H and ^{13}C) spectral studies which reveal a five coordination around the central antimony atom [112].

The complexes [(RO)P(S)S$_2$]$_3$Sb$_2$ (R=Me, Et, Pr, Pr^i, Bu, Bu^s, Bu^i, Ami, Ph and C. (h=cyclohexyl) were synthesized for the first time by the reaction of SbCl$_3$ with potassium trithiophosphates in 2:3 moleculerar ratio. Reactivity of these compounds was studied by the reactions with halogens and lewis acids such as anhydrous. AlCl$_3$. These compounds were characterized by elemental analysis, TGA as well as IR, ^{13}C NMR, ^{31}P NMR and solid state ^{27}Al NMR spectral studies [113].

A series of arylantimony derivative of analogues of dimethylcantharimide with the formulas Ar$_n$SbL$_{(5-n)}$ and Ar$_n$SbL'$_{(5-n)}$(LH=N-hydroxy-dimethyldehydrogencantharimide, L'H =N-hydroxy-dimethylcantharimide, n=3; 4; Ar=C$_6$H$_5$, 4-CH$_3$C$_6$H$_4$, 3-CH$_3$C$_6$H$_4$, 2-CH$_3$C$_6$H$_4$, 4-ClC$_6$H$_4$, 4-FC$_6$H$_4$) were synthesized and

characterized by elemental analysis, IR, ^{1}H NMR and mass spectroscopy. The crystal structures of $(C_6H_5)_4SbL$, $(4-CH_3C_6H_4)_3SbL_2$ and $(3-CH_3C_6H_4)_3SbL_2$ were detected by x-ray diffraction [114].

Antimony (III) complexes $L_nSbCl_{3-n}[HL=2-(N\text{-salicylidene})-5\text{-chlorobenzophenone}]$ were synthesized by the reactions of $SbCl_3$ with the sodium salt of 2-(N-salicylidene)-5-chlorobenzophenone (prepared in situ) in 1:1, 1:2 and 1:3 moleculerar ratios, representation. The substitution reactions of these synthesized chloro derivative were studied with alkyl xanthates. All these compounds are characterized by elemental analyses, molecular weight measurements, and spectroscopic (IR, ^{1}H and ^{13}C NMR) studies. A bidentate mode of attachment for both the Schiff base and xanthate ligands is proposed [115].

Cycloantimony(III) and cyclobismuth(III) phosphazenes I (M=Sb, Bi, R=H, TMS) were synthesized by the reactions of acyclic mono- (1), bis-(2) and tris-(3) silylated phosphazene ligands with Sb(OOCMe)$_3$ (4) and Bi(O)OOCMe (5). The reactions of (2) with (4) and (3) with (4) yielded cyclic compound I (M=Sb, R=H) and cycloantimony phosphazene complex II. The compounds I (M=Bi, R=H and TMS) were obtained by reacting (1) with (5) and (2) with (5), representation. These solid and fairly soluble compounds were characterized by elemental analysis, IR, mass and NMR spectroscopic studies.
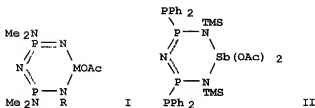
Fig. - 18 : Structure of cycloantimony phosphazene complex

1.4 SCOPE OF THE PRESENT INVESTIGATIONS:

There has been a recent enormous interest in the field of coordination chemistry of the complexes of main group metals with Schiff bases. The chemistry of Schiff bases, formed by condensation of various aldehyde with primary amine are of special interest, as they exhibit a variety of stereochemical behaviour and interesting reactions with main group metals. Schiff bases and their metal complexes are studied as model complexes of biological importance. The Schiff base metal complexes show more antibacterial, antifungal and antiviral activity than individual Schiff bases. The high reactivity, specificity and a number of applications in industry, agriculture and medicine, continue to provide the necessary impetus to the study of Schiff base complexes with transition metal.

In the present context, a brief relevant survey of literature on the Schiff base ligand and their metal complexes showed that work on Aluminium (III) and Antimony (III) metals with Schiff bases have been carried out only upto bis, tris and some mixed ligand complexes. A few chloro derivatives as well as a variety of replacement reactions with corresponding trivalent metals have also been reported.

However, chloro-bridged complexes containing Schiff bases have not yet been studied so far in details. Keeping in view it was considered worthwhile to synthesise a variety of hydrocarbon soluble chloro-bridged Schiff base metal complexes of the following type Antimony (III) complexes containing various Schiff bases $[(Cl)_2Sb(\eta^2-SB)]$, $[(Cl)Sb(\eta^2-SB)_2]$ and $[(S'B')\ (S''B'')Sb(SB)]$ where S.B. = Schiff base such as the vanillidene-2-methyl-1-amino benzene (vmabH) Salicylidene- 3-nitro-1-aminobenzene(snabH), vanillidene-1-aminobenzene (vabH), Salicylidene-anthranilic acid (saaH), vanillidene-anthranilic acid (vaaH), 4-nitrobenzylidene-2-aminophenol (nbaphH) and isatidene-3-nitro-1-aminobenzene (inabpH) with Salicylidene-1-aminobenzene (sabH) and isatidene-1-aminobenzene (iabH) for first time.

The synthesis of hydrocarbon soluble new and novel mixed ligand complexes by the reactions of monochloro Aluminium (III) and Antimony (III) complexes by the interactions with sodium phenolate, sodium tetraalkoxyaluminate and different type of Schiff

bases have been given a new dimension in the field of Schiff base chemistry.

The work described in the present thesis is a continuous programme for the investigations in the area of "Synthetic Metallo-Organic Chemistry". Dr. Dubey and Co-workers have been engaged in the synthesis and physico-chemical studies of Schiff base (derived from the condensation of various aldehydes with primary amines) complexes containing various elements of: Main group; Lanthanide and Transition metal.

Salient features of the main results achieved during the present course of investigations have been discussed under the following heads:

1. Synthesis Reaction and physicochemical Studies of Aluminium (III) Complexes containing various Schiff bases

1.21 Synthesis and physicochemical Studies of Aluminium (111) Complexes of the type $[(\mu-Cl)_2Al_2(Cl)_2(\eta2-ovmab)_2]$ $[(\mu-Cl)_2Al_2(Cl)_2$ $(\eta2-osnab)_2]$, $[(\mu-Cl)_2Al_2(\eta2-ovmab)_4]$ and $[(\mu-Cl)_2Al_2$ $(\eta2-osnab)_4]$

1.2.1.1 Reaction of $[(\mu-Cl)_2Al_2(Cl)_2(\eta2-osnab)_4]$ and $[(\mu-Cl)_2Al_2(Cl)_2$ $(\eta2-osmab)_4]$

1.2.2 Synthesis and physicochemical Studies of Aluminium (111) Complexes of the type $[(\mu\text{-}Cl)_2Al_2(Cl)_2(\eta2\text{-osmab})_2]$ $[Cl)_2Al_2(Cl)_2(\eta2\text{-ovab})_2]$, $[(\mu\text{-}Cl)_2Al_2(\eta2\text{-osmab})_2]$ and $[(\mu\text{-}Cl)_2Al_2(\eta2\text{-ovab})_4]$

1.2.2.1 Reaction of $[(\mu\text{-}Cl)_2Al_2(\eta2\text{-osmab})_4]$ and $[(\mu\text{-}Cl)_2Al_2(\eta2\text{-ovab})_4]$

1.2.3 Synthesis and physicochemical Studies of Aluminium mixed ligand complexes of the type $[(\eta2\text{-ovmab})_2\,Al(\eta2\text{-oiab})\,(\eta2\text{-osab})]$ $[(\eta2\text{-osmab})_2Al(\eta2\text{-oiab})\ (\eta2\text{-osab})]$, $[(\eta2\text{-osmab})_2Al(\eta2\text{-oiab})\ (\eta2\text{-osab})]\ [(\eta2\text{-ovab})_2Al(\eta2\text{-oiab})\ (\eta2\text{-osab})]$

1.2.3.1 Synthesis and physicochemical Studies of Aluminium mixed ligand complexes of the type $[(\eta2\text{-osaa})_2Al(\eta2\text{-oiab})$ $(\eta2\text{-osab})]\ [(\eta2\text{-ovaa})_2Al(\eta2\text{-oiab})(\eta2\text{-osab})]$, $[(\eta2\text{-onbaph})_2Al(\eta2\text{-oiab})\ (\eta2\text{-osab})]\ [(\eta2\text{-oinab})_2Al(\eta2\text{-oiab})\ (\eta2\text{-osab})]$

2. Synthesis Reactions and physico-chemical studies Antimony Complexes (III) containing Various Schiff bases

2.2.1 Synthesis and Physico-chemical studies of Antimony (111) Complexes of the types $[(Cl)_2Sb(\eta^2\text{-ovmab})]\ [(Cl)_2\ sb(osnab)]$, $[(Cl)_2Sb(\eta^2\text{-ovmab})_2]\ [(Cl)_2\ sb(osnab)]$

2.2.1.1 Reaction of $[(Cl)Sb(\eta2\text{-ovmab})]$ and $[(Cl)Sb\ (\eta2\text{-osnab})]$

2.2.2 synthesis and Synthesis and Physico-chemical studies of Antimony (111) Complexes of the type $[(Cl)_2Sb(\eta^2\text{-osmab})]$ $[(Cl)_2Sb(\eta^2\text{-osmab})_2]$and $[(Cl)_2Sb(\eta^2\text{-ovab})_2]$

2.2.2.1 Reaction of [(Cl)Sb(η2-osmab)₂] and [(Cl)Sb (η2-ovab)₂]

2.3.3 Synthesis of mixed ligand Complexes of the type[(η2-ovmab) Sb (η2-osab) (η2-oiab)] [(η2-osmab)Sb(η2-osab) (η2-oiab)], [(η2-osmab)Sb(η2-osab) (η2-oiab)] [(η2-ossa)Sb(η2-osab) (η2-oiab)] [(η2-ovaa)Sb(η2-osab) (η2-oiab)] [(η2-oinab)Sb (η2-osab)(η2-oiab)] and [(η2-onbaph) Sb(η2-osab) (η2-oiab)]

Chapter-II

RESULTS

&

DISCUSSION

*Synthesis, Reactions and Physico-chemical
Studies of Aluminium (III) Complexes
Containing Various Schiff Bases*

2.1 INTRODUCTION

Schiff base metal complexes provided interesting facts in the field of coordination chemistry due to their preparative accessibility, diversity and structural variability. The chelating properties of Schiff bases have been described, the high reactivity and specificity and number of biological application as well as catalytic activity. The Schiff bases have been used in sterioselective polymerization, various Schiff base complexes of Aluminium have been used as catalyst for synthesis. The vanillidene-2-methyl-1-aminobenzene(vmabH), salicylidene-3-nitro-1-aminobenzene(snabH), vanillidene-1-aminobenzene (vabH), salicylidene-anthranilic acid (saaH), vanillidene-anthranilicacid (vaaH), 4-nitrobenzylidene-2-aminophenol (nbaphH), isatidene-3-nitro-1-aminobenzene (inabpH) salicylidene-1-aminobenzene (sabH) and isatidene-1-aminobenzene (iabH) have been utilized to produce new hydrocarbon soluble mixed ligand complexes. However, the other aspects of coordination chemistry of Schiff bases such as -

(i)   Preparation of monochloro Schiff base complexes and their chemical reactions with various ligand produce hydrocarbon soluble bimetallic mixed ligand complexes.

(ii) Preparation of hydrocarbon soluble bimetallic mixed ligand complexes have not been explored so far.

Synthesis of hydrocarbon soluble Schiff base complexes of main group metals containing alkoxo–, phenoxo- ligands have received only scant attention. However some novel hetero (bi, ter,

tetra) metallic complexes of transition metals containing alkoxo-, aryloxo- and acetylacetonato-moieties have been reported earlier [117-124]. Keeping above in view, it is of great interest to explore the chemistry and bonding characteristics to throw light towards coordination behaviour and structural aspects of various phenoxo-bridged (binuclear) mixed ligand and alkoxo bridged (bimetallic). Schiff base complexes of group '13' specially Aluminium (III) have been synthesized.

Therefore we report here "**Synthesis, Reactions and Physico chemical Studies of Aluminium (III) Complexes Containing Various Schiff Bases**" of the type $[(\mu\text{-Cl})_2Al_2(Cl)_2(\eta^2\text{-SB})_2]$, $[(\mu\text{-Cl})_2 \, Al_2(\eta^2\text{-SB})_4]$ and $[(SB)Al(S'B') \, S''B'']$ [where S.B. = Schiff base salicylidene-2-methyl-1-aminobenzene (smabH), salicylidene-3-nitro-l-aminobenzene(snabH), salicylidene anthranilicacid (saaH), 4-nitrobenzylidene-2-aminophenol (nbaphH) and vanillidene anthranilic acid (VaaH); S'B' = isatidene-1-aminobenzene (iabH), S''B'' = salicylidene-1-aminobenzene (sabH) and η^2 = number of connectivity sites involved in bonding with metals. The structural determination of complexes have been carried out by IR, Electronic spectral data, FAB-mass (^{1}H and ^{13}C) NMR studies.

2.2 Results and Discussion

2.2.1. Synthesis and physico-chemical studies of Aluminium (III) complexes of the type $[(\mu\text{-Cl})_2Al_2(Cl)_2(\eta^2\text{-ovmab})_2]$, $[(\mu\text{-Cl})_2Al_2(Cl)_2(\eta^2\text{-osnab})_2]$ and $[(\mu\text{-Cl})_2Al_2(\eta^2\text{-vmab})_4]$ and $[(\mu\text{-Cl})_2Al_2(\eta^2\text{-osnab})_4]$.

Aluminium complexes containing Schiff bases have been prepared by the reactions of anhydrous Aluminium(III) chloride with sodium salt of vanillidene-2-methyl-1-aminobenzene (vmabH) and salicylidene-3-nitro-1-aminobenzene (snabH) in 1:1 and 1:2 molar ratios in benzene-methanol mixture, afforded complexes of types $[(\mu\text{-Cl})_2Al_2(Cl)_2(\eta^2\text{-ovmab})_2]$, $[(\mu\text{-Cl})_2Al_2(Cl)_2(\eta^2\text{-osnab})_2]$ $[(\mu\text{-Cl})_2Al_2(\eta^2\text{-ovmab})_4]$ and $[(\mu\text{-Cl})_2Al_2(\eta^2\text{-osnab})_4]$, which can be illustrated by following chemical equations.

$$AlCl_3 + Na(ovmab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)Al(ovmab)_2] + NaCl\downarrow$$
$$(I)$$

$$AlCl_3 + Na(osnab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)_2Al(osnab)] + NaCl\downarrow$$
$$(II)$$

$$AlCl_3 + 2Na(ovmab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)Al(ovmab)_2] + 2NaCl\downarrow$$
$$(III)$$

$$AlCl_3 + 2Na(osnab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)Al(osnab)_2] + 2NaCl\downarrow$$
$$(IV)$$
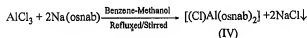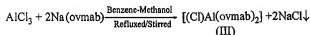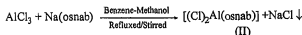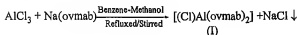
The above synthesized complexes are coloured solids and soluble in common organic solvents such as $CHCl_3$, methanol, THF, DMSO, DMF. All these complexes have been purified by recrystallisation in benzene-methanol mixture.

2.1.2 Reactions of monochloro complexes of the type $[(\mu\text{-Cl})_2\text{Al}_2(\eta^2\text{-ovmab})_4]$ and $[(\mu\text{-Cl})_2\text{Al}_2(\eta^2\text{-osnab})_4]$.

(i) *With sodium phenolate [Na(OAr)]* :

The reactions of monochloro complexes of Aluminium(III) with sodium salt of 4-nitrophenol in equimolar ratio have been carried out in benzene-methanol mixture produced phenoxo bridged complexes of the type $[(\eta^2\text{-ovmab})_4\text{Al}_2(\mu\text{-OAr})_2]$ and $[(\eta^2\text{-osnab})_4\text{Al}_2(\mu\text{-OAr})_2]$ which can be represented by the following chemical equations.
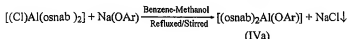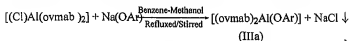
$$[(\text{Cl})\text{Al}(\text{ovmab})_2] + \text{Na}(\text{OAr}) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(\text{ovmab})_2\text{Al}(\text{OAr})] + \text{NaCl} \downarrow$$
$$\text{(IIIa)}$$

$$[(\text{Cl})\text{Al}(\text{osnab})_2] + \text{Na}(\text{OAr}) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(\text{osnab})_2\text{Al}(\text{OAr})] + \text{NaCl} \downarrow$$
$$\text{(IVa)}$$

These complexes are coloured solids and are soluble in common organic solvents such as methanol and CHCl$_3$. These complexes have been purified by recrystallisation in benzene methanol mixture. Some physical properties of these complexes are listed in table [5-6].

(ii) *With sodium tetralkoxyaluminate [Na(Al(OPr^i)$_4$]* :

The reaction of monochloro complexes of Aluminium (III) such as $[(\mu\text{-Cl})_2\text{Al}_2(\eta^2\text{-ovmab})_4]$, $[(\mu\text{-Cl})_2\text{Al}_2(\eta^2\text{-osnab})_4]$ containing Schiff bases have been carried out with sodium salt of tetra isopropoxyaluminte $[\text{Na}_4^{\downarrow}\{\text{Al}(\text{OPr}^i)_4\}]$ in 1:1 stiochiometric ratio in benzene-methanol mixture obtained complexes of the type $[(\eta^2\text{-ovmab})_2\text{Al}\{\text{Al}(\text{OPr}^i)_4\}]$ and $[(\eta^2\text{-osnab})_2\text{Al}\{\text{Al}(\text{OPr}^i)_4\}]$, which can be demonstrated as follows :

$$[(\text{Cl})\text{Al}(\text{ovmab})_4] + \text{Na}\{\text{Al}(\text{OPr}^i)_4\} \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(\text{ovmab})_2\text{Al}\{\text{Al}(\text{OPr}^i)_4\}] + \text{NaCl} \downarrow$$
$$\text{(IIIb)}$$

$$[(Cl)Al(osnab)_2] + Na\{Al(OPr^i)_4\} \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(osnab)_2Al\{Al(OPr^i)_4\}] + NaCl\downarrow$$
(IVb)
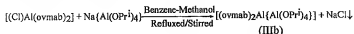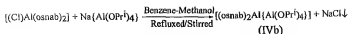
These complexes are coloured crystalline solid and are finally soluble in common organic solvents such as methanol, $CHCl_3$ THF, DMF, DMSO and purified by recrystallisation in benzene-methanol mixture.

2.2.2 Synthesis and physico-chemical studies of Aluminium (III) complexes of the types $[(\mu\text{-}Cl)_2Al_2(Cl)_2(\eta^2\text{-osmab})_2]$, $[(\mu\text{-}Cl)_2Al_2(Cl)_2(\eta^2\text{-ovab})_2]$, $[(\mu\text{-}Cl)_2Al_2(\eta^2\text{-osmab})_4]$ and $[(\mu\text{-}Cl)_2Al_2(\eta^2\text{-ovab})_4]$.

When a hot solution of anhydrous $AlCl_3$ in benzene was added slowly to the freshly prepared sodium salt of salicylidene-2-methyl aminobenzene(smabH) and vanillidene-1-aminobenzene (vabH) in 1:1 and 1:2 molar ratios, afforded complexes of the types $[(\mu\text{-}Cl)_2Al_2(Cl)_2(\eta^2\text{-osmab})_2]$, $[(\mu\text{-}Cl)_2Al_2(Cl)_2(\eta^2\text{-ovab})_2]$, $[(\mu\text{-}Cl)_2Al_2(\eta^2\text{-osmab})_4]$ and $[(\mu\text{-}Cl)_2Al_2(\eta^2\text{-ovab})_4]$, which can be demonstrated by the following chemical equations:
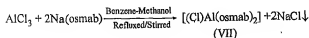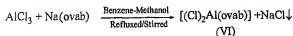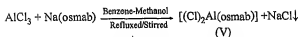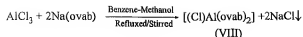
$$AlCl_3 + Na(osmab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)_2Al(osmab)] + NaCl\downarrow$$
(V)

$$AlCl_3 + Na(ovab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)_2Al(ovab)] + NaCl\downarrow$$
(VI)

$$AlCl_3 + 2Na(osmab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)Al(osmab)_2] + 2NaCl\downarrow$$
(VII)

$$\text{AlCl}_3 + 2\text{Na(ovab)} \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [\text{(Cl)Al(ovab}_2] + 2\text{NaCl} \downarrow$$

$$(\text{VIII})$$

These freshly prepared complexes are found to be coloured solid soluble in common organic solvents such as methanol benzene, CHCl$_3$, THF, DMSO, DMF. All these complexes has been purified by recrystallisation in benzene-methanol mixture. Some of their phy2sical properties are given in Table [5-6].

2.2.2.1 Reactions of $[(\mu\text{-Cl})_2\text{Al}_2(\eta^2\text{-osmab})_4]$ and $[(\mu\text{-Cl})_2\text{Al}_2(\eta^2\text{-(ovab})_4].$

(i) With sodium phenolate[Na(OAr)] :

The chlorine replacement reaction of monochloro Aluminium(III) complexes such as $[(\mu\text{-Cl})_2\text{Al}_2(\eta^2\text{-osmab})_4]$ and $[(\mu\text{-Cl})_2\text{Al}_2(\eta^2\text{-ovab})_4]$ with sodium salt of 4-nitrophenol in 1:1 stoichiometric ratio in benzene-methanol mixture, produces complexes of the type $[(\mu\text{-OAr})_2\text{Al}_2(\eta^2\text{-osmab})_4]$ and $[(\mu\text{-OAr})_2\text{Al}_2(\eta^2\text{-ovab})_4]$, which have been demonstrated by the following chemical equations.

$$[(\text{Cl})\text{Al (osmab)}_2] + \text{Na(OAr)} \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [\text{(osmab)}_2\text{Al (OAr)}] + \text{NaCl} \downarrow$$

$$(\text{VIIa})$$

$$[(\text{Cl})\text{Al(ovab)}_2] + \text{Na(OAr)} \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [\text{(ovab)}_2\text{Al (OAr)}] + \text{NaCl} \downarrow$$

$$(\text{VIIIa})$$
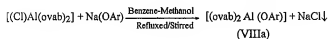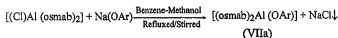
These phenoxo bridged complexes are coloured solids and soluble in common organic solvents like methanol, THF, CHCl$_3$ and purified by recrystallization in the solution of benzene-methanol mixture. Some of their physical properties are listed in Table [5-6].

(ii) With sodium tetraisopropoxyaluminate $Na[\{Al(OPr^i)_4\}]$:

The chloride replacement reaction of monochloro Aluminium(III) complexes such as $[(\mu\text{-Cl})_2Al_2(\eta^2\text{-osmab})_4]$ and $[(\mu\text{-Cl})_2Al_2(\eta^2\text{-ovab})_4]$ have been carried out with sodium salt of tetraisopropoxyaluminate $[Na\{Al(OPr^i)_4\}]$ in 1:1 molar ratio in the presence of benzene-methanol mixture, produce alkoxo bridged complexes of the type $[(\eta^2\text{-osmab})_2Al(\mu\text{-OPr}^i)_2\{Al(\mu\text{-OPr}^i)_2\}]$ and $[(\eta^2\text{-OVAB})_2Al(\mu\text{-OPr}^i)_2\{Al(\mu\text{-OPr}^i)_2\}]$, which can be shown by following chemical equations.

$$[(Cl)Al(osmab)_2] + Na\{Al(OPr^i)_4\} \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(osmab)_2Al\{Al(OPr^i)_4\}] + NaCl\downarrow$$
$$(VIIb)$$

$$[(Cl)Al(ovab)_2] + Na\{Al(OPr^i)_4\} \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(ovab)_2Al\{Al(OPr^i)_4\}] + NaCl\downarrow$$
$$(VIIIb)$$
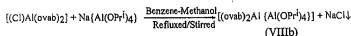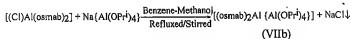
These complexes are coloured solid and fairly soluble in methanol, n hexane, CHCl₃, THF, DMF, DMSO and purified by recrystallisation in n hexane-benzene.

2.3.3. Synthesis and physico-chemical studies of mixed ligand complexes of the Aluminium(III) of the type $[(SB)Al(S'B')(S''B'')]$.

The mixed ligand complexes of the type $[(SB)Al(S'B')(S''B'')]$ have been prepared by interactions of freshly prepared dichloro $[(Cl_2)Al(SB)]$ complexes of Aluminium (III) with sodium salt of ligand $Na(S'B')$ and $Na(S''B'')$ in 1:1:1 molar ratio in benzene-methanol mixture {SB=vmabH, snabH, vabH, saaH, vaaH, inabH, nbaphH, S'B'=iabH and S''B''=sabH)}, afforded mixed ligand

complexes of the following type represented by following chemical equations.

$$[(Cl)_2Al(ovmab)] + Na(olab) + Na(osab) \xrightarrow{\text{Benzene-Methanol}}_{\text{Refluxed/Stirred}} [(ovmab)Al(olab)(osab)] + 2NaCl\downarrow$$
(IX)

$$[(Cl)_2Al(osmab)] + Na(olab) + Na(osab) \xrightarrow{\text{Benzene-Methanol}}_{\text{Refluxed/Stirred}} [(osmab)Al(olab)(osab)] + 2NaCl\downarrow$$
(X)

$$[(Cl)_2Al(osmsb)] + Na(olab) + Na(osab) \xrightarrow{\text{Benzene-Methanol}}_{\text{Refluxed/Stirred}} [(osmsb)Al(olab)(osab)] + 2NaCl\downarrow$$
(XI)

$$[(Cl)_2Al(ovab)] + Na(olab) + Na(osab) \xrightarrow{\text{Benzene-Methanol}}_{\text{Refluxed/Stirred}} [(ovab)Al(olab)(osab)] + 2NaCl\downarrow$$
(XII)

$$[(Cl)_2Al(osaa)] + Na(olab) + Na(osab) \xrightarrow{\text{Benzene-Methanol}}_{\text{Refluxed/Stirred}} [(osaa)Al(olab)(osab)] + 2NaCl\downarrow$$
(XIII)

$$[(Cl)_2Al(ovaa)] + Na(olab) + Na(osab) \xrightarrow{\text{Benzene-Methanol}}_{\text{Refluxed/Stirred}} [(ovaa)Al(olab)(osab)] + 2NaCl\downarrow$$
(XIV)

$$[(Cl)_2Al(oinab)] + Na(olab) + Na(osab) \xrightarrow{\text{Benzene-Methanol}}_{\text{Refluxed/Stirred}} [(oinab)Al(olab)(osab)] + 2NaCl\downarrow$$
(XV)

$$[(Cl)_2Al(onbaph)] + Na(olab) + Na(osab) \xrightarrow{\text{Benzene-Methanol}}_{\text{Refluxed/Stirred}} [(onbaph)Al(olab)(osab)] + 2NaCl\downarrow$$
(XVI)

These mixed ligand complexes are coloured solids, soluble in common organic solvents and are purified by recrystallisation in benzene methanol mixture. Some of their properties are collected in table [5-6].

Table-5

Physical properties of Aluminium (III) complexes containing Schiff bases

Sl. No.	Complexes	Physical State	mp(°C)
1.	$[(\mu\text{-Cl})_2Al_2(Cl)_2(\eta^2\text{-ovmab})_2]$	Light brown solid	147
2.	$[(\mu\text{-Cl})_2Al_2(Cl)_2(\eta^2\text{-osnab})_2]$	Light yellow	137
3.	$[(\mu\text{-Cl})_2Al_2(\eta^2\text{-ovmab})_4]$	Black solid	110
4.	$[(\mu\text{-Cl})_2Al_2(\eta^2\text{-osnab})_4]$	Brown solid	125
5.	$[(\mu\text{-OAr})_2Al_2(\eta^2\text{-ovmab})_4]$	Dirty yellow	205
6.	$[(\mu\text{-OAr})_2Al_2(\eta^2\text{-osnab})_4]$	Light green solid	208
7.	$[(\eta^2\text{-ovmab})_2Al(\mu\text{-OPr}^i)_2\{Al_2(OPr^i)_2]$	Light yellow	304[a]
8.	$[(\eta^2\text{-osnab})_2Al(\mu\text{-}$ $OPr^i)_2\{Al(OPr^i)_2]$	Brownish black solid	292[a]
9.	$[(\eta^2\text{-ovab})Al(\eta^2\text{-osnab})(\eta^2\text{-ovab})]$	Green yellow solid	168
10.	$[(\eta^2\text{-osnab})Al(\eta^2\text{-osab})(\eta^2\text{-ovab})]$	Pink coloured solid	172
11.	$[(\eta^2\text{-osmab})Al(\eta^2\text{-osnab})(\eta^2\text{-oiab})]$	Green yellow solid	165
12	$[(\eta^2\text{-vab})Al(\eta^2\text{-osab})(\eta^2\text{-oiab})]$	Dark yellow solid	175

a = Neither melted nor decomposed

Table-6

Physical properties of Aluminium (III) complexes containing Schiff bases

Sl. No.	Complexes	Physical State	m.p.(°C)
1.	$[(\mu\text{-Cl})_2Al_2(Cl)_2(\eta^2\text{-osmab})_2]$	Light yellow solid	148
2.	$[(\mu\text{-Cl})_2Al_2(Cl)_2(\eta^2\text{-ovab})_2]$	Brownish yellow solid	151
3.	$[(\mu\text{-Cl})_2Al_2(\eta^2\text{-osmab})_4]$	Brown solid	158
4.	$[(\mu\text{-Cl})_2 Al_2(\eta^2\text{-ovab})_4]$	Light brown solid	210
5.	$[(\mu\text{-OAr})_2 Al_2(\eta^1\text{-osmab})_4]$	Leaf green solid	194
6.	$[(\mu\text{-OAr})_2 Al_2(\eta^1\text{-ovab})_4]$	Raddish yellow	207
7.	$[(\eta^2\text{-osmab})_2Al(\mu\text{-OPr}^i)_2\{Al_2(OPr^i)_2]$	Yellowish green solid	295ᵃ
8.	$[(\eta^2\text{-ovab})_2Al(\mu\text{-OPr}^i)_2\{Al_2(OPr^i)_2]$	Black	305ᵃ
9.	$[(\eta^2\text{-ossa})Al_2(\eta^2\text{-osab}) (\eta^2\text{-oiab})]$	Dark brown solid	170
10.	$[(\eta^2\text{-ovaa})Al_2(\eta^2\text{-osab}) (\eta^2\text{-ovab})]$	Pink solid	183
11.	$[(\eta^2\text{-oinab})Al_2(\eta^2\text{-osab}) (\eta^2\text{-oiab})]$	Pinkish yellow solid	174
12.	$[(\eta^2\text{-onbph})Al_2(\eta^2\text{-osab}) (\eta^2\text{-oiab})]$	Brownish yellow solid	193

a = Neither melted nor decomposed

2.2.4 Spectral studies of Aluminium (III) complexes containing Schiff bases.

Infrared, Electronic (U.V.-visible), FAB-mass and Nuclear Magnetic Resonance studies (^{1}H&^{13}C) have been recorded for Aluminium (III) complexes, in order to understand the coordination behaviour around Aluminium(III). The important conclusion drawn from these analytical techniques are furnished below systematically, which in turn have been utilized in predicting structural feature of the complexes under study.

2.2.4.1 Infrared Spectral Studies :

Infrared spectra of Aluminium (III) complexes contain Schiff bases such as vanillidene-2-methyl-1-amino benzene (vmabH) Salicylidee-3-nitro-1-aminobenzene(snabH), vanillidene-1-aminobenzene (vabH) Salicylidene-anthranilic acid (saaH), vanillidene-anthranilic acid (vaaH), 4-nitrobenzylidene-2-aminophenol (nbaphH), isatidene-3-nitro-1-aminobenzene (inabpH), salicylidene-1-aminobenzene (sabH) and isatidene-1-aminobenzene (iabH) have been recorded in nujol null in the range 4000-200 cm^{-1} and are summarised in Table [7].

In IR spectra presence of Schiff base moieties indicated by the appearance of absorption band at 1625-1614 cm^{-1} in free ligand [125] is characteristic for $\nu_{(C-N)}$ band ,in the complexes this band shifter to lower wave number at (1614-1595) cm^{-1} indicates coordination of azomethine nitrogen with metal ion.

The Schiff bases generally (containing phenolic group displayes two band ~3564-3329 cm^{-1} and at 1398-1310 cm^{-1} which have been specified for $\nu_{(O-H)}$ stretching and $\delta_{(O-H)}$ deformatio frequencies respectively. These frequencies disappeared in th spectra of complexes of Aluminium (III) suggesting [126 deprotonation of phenolic OH after chelation with metal ion.

The $\nu_{(C-O)}$ (phenolic) bands were observed at 1277-1269 cm in all the Schiff bases. These bands shifted to higher wave number i complexes at 1293-1270 cm^{-1} suggesting coordination throug phenolic oxygen.

The dichloro and monochloro complexes $[(\mu\text{-Cl})_2Al_2(Cl)_2(\eta^2\text{-ovmab})_2](I)$, $[(\mu\text{-Cl})_2Al_2(Cl)_2(\eta^2\text{-osnab})_2](II)$, $[(\mu\text{-Cl})_2Al_2(Cl)_2(\eta^2\text{-osmab})_2](V)$, $[(\mu\text{-Cl})_2Al_2(Cl)_2 \quad (\eta^2\text{-ovab})_2](VI)$, $[(\mu\text{-Cl})_2Al_2(\eta^2\text{-osnab})_4](IV)$, $[(\mu\text{-Cl})_2Al_2(\eta^2\text{-ovmab})_4](III)$, $[(\mu\text{-Cl})_2Al_2(\eta^2\text{-osmab})_4](VII)$, $[(\mu\text{-Cl})_2Al_2(\eta^2\text{-ovab})_4](VIII)$ display sharp IR bands for complexes (I), (II), (V) 306 (m), 286(s), 292, 288(s) for IV, III, 324, 294, 288(s) 312, 296, 286(s), VII, 324, 286(s), 322, 286, which have been appeared for $\nu_{(Al\text{-}Cl)}$ vibration.

In monochloro Aluminium (III) complexes, the terminal chloride $\nu_{t(Al\text{-}Cl)}$ stretching frequency usually occurs at higher region 345-310 cm^{-1} than the bridging metal chloride $\nu_{b(M\text{-}Cl)}$ stretching frequencies, which occurs in the lower region ~190-295 cm^{-1} due to delocalization of electrons in chelate ring. In these complexes (III, IV, VII, VIII) absence of sharp band in the range 345-310cm^{-1} suggest the absence of terminal chlorine atom and the strong band in the region 190-295 cm^{-1} identified for $\nu_{Al\text{-}Cl}$ stretch for bridging chlorine. On the basis of above finding following representative structure have been suggested.
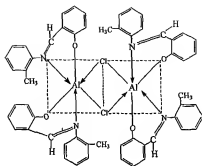
Fig.19 Proposed structure of [(μ-Cl)₂Al₂(η²-osnab)₄]

In the dichloro complexes (I, II, IV, V) the presence of strong band in the region 345-310 cm⁻¹ and 295-190 cm⁻¹ give information that it contain both terminal and bridging chlorine. On the basis of these studies following representative structures have been suggested.
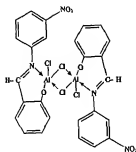
Fig. 20 Proposed structure of [(μ-Cl)₂Al₂(Cl)₂(η¹-osnab)₂]

The IR spectra of phenoxo-bridge complexes [(μ-OAr)₂Al₂(η²-ovmab)₄](IIIa), [(μ-OAr)₂Al₂(η²-osnab)₄](IVa), [(μ-OAr)₂Al₂(η²-osmab)₄] (VIIa), [(μ-OAr)₂Al₂(η²-ovab)₄](VIIIa). The

$v_{(C-O)}$ appearing at 1277-1269 cm^{-1} in free ligand shifted to higher frequency region (by~11-21 cm^{-1}) in complexes assigned to $v_{(C-O)}$ (phenolic) stretching [128-129] evidence of phenolic oxygen bridge in complexes.
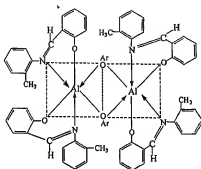
Fig. 21 Proposed structure of [(μ-OAr)2Al2(η2-osmab)4]

The IR spectra of alkoxo-bridged complexes [(η²-ovmab)₂ Al₂(μ-OPr^i)₂ {Al₂(μ-OPr^i)₂}](III-b), [(η²-osnab)₂Al₂(μ-OPr^i)₂ {Al₂(μ-OPr^i)₂}](IV-b), [(η²-osmab)₂Al₂(μ-OPr^i)₂{Al(μ-OPr^i)₂}](VII-b), [(η²-ovmab)₂Al₂(μ-OPr^i)₂ {Al(μ-OPr^i)₂}](VIII-b), exhibited characteristic frequency for metal alkoxy group $v_{(Al-O-Al)}$ band observed [130-134] in the region 751-735 cm^{-1}. The strong intensity band observed in the region 1025-1015 cm^{-1}, which may be specified for $v_{(C-O)}$ of bridging and termination isopropoxy groups.

The infrared spectra of mixed ligand complexes of Aluminium (III) [(η²-ovmab)Al(η²-osab)(η²-oiab)] IX, [(η²-osab)Al(η²-ovab)(η²-osab)]

X, [(η^2-osmab)Al(η^2-oiab)(η^2-osab)] XI, and [(η^2-ovab)Al(η^2-oiab)(η^2-osab)] on the basis of IR spectral studies following structure have been suggested for mixed ligand complexes.
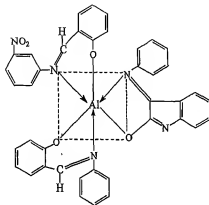
Fig. 22 Proposed structure of mixed ligand complexes [(η^2-osnab)Al(η^2-osab)(η^2-oiab)]

All the complexes shows characteristic IR frequency in the range 610-587 cm^{-1} which may be assigned to Al-O vibration [127] the band (475-450)cm^{-1} observed in the Aluminium complexes may be attributed to $v_{(Al-N)}$ vibration.

(76)

Table-7

Characteristic IR Frequencies (cm⁻¹) of Schiff bases

SL.No.	Schiff Bases		$\nu_{(C=N)}$	$\nu_{(C-O)}$ Phenolic	$\delta_{(O-H)}$ Stretching	$\delta_{(O-H)}$ Deformation
1.	Vanillidene-2-methyl-1-aminobenzene	(vmabH)	1617	1272	3564	1310
2.	Salicylidene-2-methyl-1-aminobenzene	(smabH)	1620	1275	3353	1360
3.	Salicylidene-3-nitro-1-aminobenzene	(snabH)	1614	1277	3343	1371
4.	Vanillidene-3-methyl-1-aminobenzene	(vabH)	1615	1274	3445	1350,1379
5.	Salicylidene-1-aminobenzene	(sabH)	1618	1269	3330	1350,1379
6.	Isatidene-3-nitro-1-aminobenzene	(inabH)	1623,1589	1272	3329	1344,1374
7.	Isatidene-1-aminobenzene	(iabH)	1618	1275	3453	1389
8.	Salicylidene-anthranilic acid	(saaH)	1625	1273	3353	1358
9.	Vanillidene-anthranilic acid	(vaaH)	1622	1270	3344	1362
10.	4-nitrobenzylidene-2-aminophenol	(nbapbH)	1618	1274	3348	1368

(77)

Table - 8

Characteristic IR frequencies (cm⁻¹) of Aluminium (III) complexes containing Schiff bases

Sl. No.	Complexes		νAl-N	νAl-O	νC-O Phenolic	νC=N	νAl-O Terminal	νAl-O Bridging	νC-O-Al
1.	[(μ-Cl)₂ Al₂(Cl)₂(η²-ovmnsab)₂]	(I)	450	580	1288	1604	342	198	-
2.	[(μ-Cl)₂ Al₂(Cl)₂(η²-osnab)₂]	(II)	455	604	1297	1610	322	200	-
3.	[(μ-Cl)₂ Al₂(Cl)₂(η²-osnab)₂]	(III)	468	610	1287	1598	-	207	-
4.	[(μ-Cl)₂ Al₂(η²-osnab)₂]	(IV)	470	587	1285	1606	-	210	-
5.	[(μ-OAr)₂ Al₂(η²-ovmnsab)₂]	(IIIa)	471	595	1291	1598	-	-	-
6.	[(μ-OAr)₂ Al₂(η²-osnab)₂]	(IVa)	495	608	1289	1608	-	-	1015-1025t, 735-151b
7.	[(η²-ovmnsab)₂Al (μ-OPr³)₂ (Al₂(OPr³)₂]	(IIIb)	500	588	1286	1603	-	-	1007-1022t, 725-751b
8.	[(η²-osnab)₂Al₂(μ-OPr³)₂(Al(OPr³)₂]	(IVb)	492	609	1290	1607	-	-	-

t- terminal b-bridging (Isopropoxy group)

Table- 9

Characteristic IR frequencies (cm⁻¹) of Aluminium (III) complexes containing Schiff bases

Sl. No.	Complexes		ν_{AlN}	ν_{AlO}	ν_{C-O} Phenolic	ν_{C-N}	ν_{AlCl} Terminal	ν_{AlCl} Bridging	$\nu_{Al-O-Al}$
1.	[(μ-Cl)₂Al₂(Cl)₂(η²-osmalo)₄]	(V)	450	587	1291	1612	345	185	-
2.	[(μ-Cl)₂ Al₂(Cl)₂(η²-ovalo)₄]	(VI)	455	590	1294	1598	322	195	-
3.	[(μ-Cl)₂ Al₂(η²-osmalo)₃]	(VII)	461	595	1289	1614	-	198	-
4.	[(μ-Cl)₂ Al₂(η²-ovalo)₃]	(VIII)	467	600	1287	1604	-	200	-
5.	[(μ-OAr)₂ Al₂(η²-osmalo)₄]	(VIIa)	498	605	1287	1613	-	-	-
6.	[(μ-OAr)₂ Al₂(η²-ovalo)₄]	(VIIIa)	452	610	1291	1609	-	-	-
7.	[(η²-osmalo)₂Al (μ-OPⁱ₂)₂ {Al(OPⁱ₂)}]	(VIIb)	471	592	1295	1610	-	-	1020-1030ᵗ / 725-751ᵇ
8.	[(η²-ovalo)₂Al₂(μ-OPⁱ₂){Al(OPⁱ₂)}]	(VIIIB)	448	608	1296	1608	-	-	1010-1025ᵗ / 730-751ᵇ

t- terminal b-bridging (Isopropoxy group)

Table-10

Characteristic IR frequencies (cm⁻¹) of mixed ligand complexes of Aluminium(III) containing Schiff bases

Sl. No.	Complexes		ν_{M-N}	ν_{M-O}	ν_{C-O} Phenolic	$\nu_{C=N}$
1.	[(η³-ovmnb)Al(η³-osab) (η²-olab)]	(IX)	450	582	1289	1610
2.	[(η³-omnb)Al(η³-osab) (η²-olab)]	(X)	455	588	1288	1608
3.	[(η³-omnb)Al(η³-osab) (η²-olab)]	(XI)	458	590	1282	1602
4.	[(η³-ovab)Al(η³-osab) (η²-olab)]	(XII)	459	570	1290	1604
5.	[(η³-osab)Al(η³-osab) (η²-olab)]	(XIII)	462	572	1289	1606
6.	[(η³-ovab)Al(η³-osab) (η²-olab)]	(XIV)	468	580	1296	1607
7.	[(η³-olnb)Al(η³-osab) (η²-olab)]	(XV)	500	610	1293	1603
8.	[(η³-onbnb)Al (η²-osab) (η²-olab)]	(XVI)	495	608	1290	1606

2.2.4.2 Electronic Spectroscopy

The electronic spectra of Schiff bases[34] exhibit three bands around 40000, 31746 and 25000cm^{-1}. The band around 40000 and 31746 cm^{-1} are probably due to π - π* transitions of benzenoid ring conjugated with double bond of azomethine group and the band around 25000 cm^{-1} may be due to the n→π* transition of bonding electrons present in the azomethine group in the Aluminium(III) complexes. There is no shift in the position of first two bands. These bands in complexes are slightly broader in nature probably due to presence of two different types of Schiff bases. The band around 25000 cm^{-1} shows bathochromic shifts in between 25000-23800 in the complexes due to the coordination of nitrogen of azomethine group with central Aluminium atom. Details are summarized in Table [11].

Table-11

Electronic (U.V.-visible) spectral data of Aluminium(III) complexes containing Schiff bases

Sl. No.	Complexes	Transitions (cm⁻¹)	
		n → π*	π → π*
1.	[(μ-Cl)₂ Al₂(ClO)(η³-osmab)₂]	25700	39000
2.	[(μ-Cl)₂ Al₂(ClO)(η³-ovab)₂]	25350	31000
3.	[(μ-Cl)₂ Al₂(η³-osmab)₂]	25620	38000
4.	[(μ-Cl)₂ Al₂(η³-ovab)₂]	24900	31275
5.	[(μ-OAc)₂ Al₂(η³-smab)₂]	25840	31532
6.	[(μ-OAc)₂ Al₂(η³-ovab)₂]	25750	31662
7.	[(η³-osmab)₂Al (μ-OP³)₂ {Al₂(OP³)₂]	25189	39182
8.	[(η³-ovab)₂Al(μ-OP³)₂{Al(OP³)₂]	25278	38372
9.	[(η³-osmab)Al(η³-osab) (η³-slab)]	25735	40342
10.	[(η³-ovab)Al(η³-osab) (η³-slab)]	25343	34175

2.2.4.3 Proton Magnetic Resonance Spectroscopy

The proton magnetic resonance spectra of these complexes recorded in deuterated chloroform and in DMSO-d$_6$, the spectra are quiet complicated due to spin-spin splitting of different groups and are not easy to interpret however a comparison of spectra of ligand with that of the complexes can lead to the following conclusions. Table [12-13].

(i) A strong signal appeared in the region δ13.6-13.8 ppm may be assigned to OH proton of Schiff base, [135] however this signal disappear in the spectra of corresponding Aluminium complexes showing that deprotonation of OH subsequently involved in the Al-O bond formation.

(ii) The proton signal appeared in the region δ8.10 ppm in free ligand due to azomethine proton this signal shifted down field in Aluminium (III) complexes from δ8.10 to 9.25 ppm. These data may provide support that azomethine nitrogen involved in coordination Aluminium (III) atom [136].

(iii) The chemical shift due to aromatic ring proton appears in between δ7.8-8.4 ppm in ligands, which may be shifted slightly down field in the complexes may be due to decrease in electron density after formation of complex.

(iv) The complexes containing vanillidene Schiff bases showed an extra proton signal due to m-OCH$_3$ group [135] (I, III, IIIa, IIIb, IV, VII, VIIIa, VIIIb, IX, XII, XIV) observed near δ3.50-3.90 ppm.

(v). A doublet obtained at δ11.2 ppm in the spectra of isatin derived ligand which may be disappeared in the complexes (IX, X, XI, XII, XIII, XIV, XV, XVI) further suggesting enolization of keto group and Al-O bond formation occurred.

(vi) The methine protons of terminal and bridging [137] isopropoxy group are observed in complexes (IIIb, VIb, VIIb, VIIIb) at δ3.90 to 3.99 ppm. and δ4.06 to 4.25 ppm respectively. The data may suggest that two Aluminium atom are bonded with each other through [138] isopropoxy bridged structure.

(vii). The signal due to other protons in Schiff bases and their shift in their corresponding Aluminium (III) are compatible with literature data. On the basis of above studies following structure will be assigned.
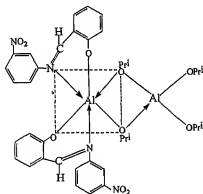
Fig. 23 Proposed structure of [(η²-osnab)₂Al(μ-OPrⁱ)₂Al{(OPrⁱ)₂}]

Table -12

Proton magnetic resonance spectra of Aluminium(III) complexes (δ, ppm) containing Schiff bases

Sl. No.	Compound	Acetaldehyde	Benzene	-OH	m-OCH₃	Isopropoxide	
						Terminal	Bridging
1.	vmabH	8.45	6.8-7.8	13.20	-	-	-
2.	[(μ-Cl)₂ Al₂(Cl)₂(η¹-ovmab)₂]	9.66	7.2-8.1	-	3.81	-	-
3.	[(μ-Cl)₂ Al₂(Cl)₂(η²-osmab)₂]	9.76	7.1-8.0	-	-	-	-
4.	[(μ-Cl)₂ Al₂(η¹-ovmab)₄]	9.78	6.9-7.9	-	3.89	-	-
5.	[(μ-Cl)₂ Al₂(η²-osmab)₄]	9.46	6.9-7.7	-	-	-	-
6.	[(μ-OAc)₂ Al₂(η¹-ovmab)₄]	9.57	7.0-8.0	-	3.93	-	-
7.	[(μ-OAc)₂ Al₂(η²-osmab)₄]	9.66	6.8-8.0	-	-	-	-
8.	[(η²-ovmab)₂Al(μ-OPrⁱ)₂Al(OPrⁱ)₂]	9.58	7.8-8.0	-	3.96	3.72-3.99	4.02-4.26
9.	[η¹-osmab)₂Al(μ-OPrⁱ)₂Al(OPrⁱ)₂]	9.53	6.9-7.9	-	-	3.77-3.88	4.10-4.28
10.	[(η²-ovab)₂Al(η¹-osab) (η²-sab)]	9.59	6.8-7.9	-	3.86	-	-

Table–13

Proton magnetic resonance spectra of Aluminium(III) complexes (δ, ppm) containing Schiff bases

Sl. No.	Compound	HC=N	Benzene	-OH	m-OCH₃	Isopropoxide Terminal	Isopropoxide Bridging
1.	smnbH	8.30	6.8-7.8	13.40	-	-	-
2.	[(μ-Cl)₂ Al₂(Cl)₂(η²-osmnb)₂]	9.59	6.9-7.8	-	-	-	-
3.	[(μ-Cl)₂ Al₂(Cl)₂(η²-ovnb)₂]	9.52	6.9-7.9	-	3.81	-	-
4.	[(μ-Cl)₂ Al₂(η²-osmnb)₂]	9.64	6.8-7.4	-	-	-	-
5.	[(μ-Cl)₂ Al₂(η²-ovnb)₂]	9.72	7.0-8.0	-	3.91	-	-
6.	[(μ-OAr)₂ Al₂(η²-smnb)₂]	9.78	6.9-7.7	-	-	-	-
7.	[(μ-OAr)₂Al₂(η²-ovnb)₂]	9.62	6.9-7.9	-	3.82	-	-
8.	[(η²-osmnb)₂Al₂(μ-OPr)₂][Al(OPr)₂]	9.67	7.1-7.6	-	-	3.76-3.99	4.04-4.26
9.	[(η²-ovnb)₂Al₂(μ-OPr)₂][Al(OPr)₂]	9.73	7.2-8.1	-	3.92	3.70-3.88	4.10-4.28
10.	[(η²-smnb)Al(η²-osnb)(η²-visnb)]	9.71	6.8-7.8	-	-	-	-

2.2.4.4 ^{13}C NMR Spectral Studies

The ^{13}C NMR spectra of these complexes showes characteristic resonance due to the alkoxy, hydroxy, methoxy, phenyl and azomethine groups. The spectral studies of metal complexes should be interpreted by comparison of spectra of ligands, following conclusions may be drawn mentioned below Table [14-15].

(i) The ligand ^{13}C NMR studies showed reasonable shift in the phenolic carbon from δ149.84 to 159.64 ppm. The down field shift in phenolic carbon atom showing coordination may occurs from oxygen and form Al-O bond.

(ii) The Schiff bases showed sharp singlet at δ151.24 ppm for azomethine carbon atom which may shifted down field in the complexes δ160.15 ppm showing coordination of azomethine nitrogen with Aluminium (III) atom [138].

(iii) In Aluminium (III) complexes signal appeared in the region δ125.62, 138.50, 122.70 ppm, which may be assigned to the three different carbon atom, of benzene ring of ligand moiety. There is no appreciable shift found in the carbon of benzene ring [139].

(iv) In the ^{13}C NMR spectral data of ligand (Isatine derivative) and their complexes (IX, X, XI, XII, XIII, XIV, XV, XVI), the down field shift in the position of amido carbon from δ166 to δ170 ppm clearly indicated that covalent bond formation may occur through to enolic form of ligand [140].

(v)   A sharp signal obtained for methine carbon of the terminal and bridging isopropoxy groups are observed in complexes (IIIb, VIb, VIIb, VIIIb) at δ60.18 to 60.52 ppm and δ61.16 to 64.42 ppm respectively. The data may suggest that two Aluminium atoms are bonded to each other through isopropoxy bridged carbon atom [138].

(vi)   A sharp singlet showed downfield shift due of -COOH carbon atom from δ170 to 162 ppm in comparison to free ligand indicating coordination may occur through carboxy oxygen in monodentate way [141].

(vii)   Vanillidene Schiff bases Aluminium (III) complexes (I, III, IIIa, IIIb, IV, VII, VIIIa, VIIIb, IX, XII, XIV) shows singlet at δ54.1 ppm, which is characteristic of OCH$_3$ group [142].

Table 14

^{13}C Nuclear magnetic resonance data (δ, ppm) Aluminium(III) complexes containing Schiff bases

Sl. No.	Complexes	-OH	Azomethine CH=N	Aromatic carbon	Amido carbon	-COOH	OCH₃	Isopropoxide	
								Terminal	Bridging
1.	vmabH	149.04	151.24	138.20,125.40, 122.60,	-	-	53.09	-	-
2.	[(μ-Cl)₂Al₂ (Cl)₂(η²-ovmab)₂]	160.12	152.30	137.40,123.60, 121.60,	-	-	53.05	-	-
3.	[(μ-Cl)₂Al₂ (Cl)₂(η²-osmab)₂]	154.54	153.40	147.60,124.80, 123.70,	-	ʅ	-	-	-
4.	[(μ-Cl)₂Al₂ (η²-ovmab)₂]	157.89	154.60	148.10,125.90, 121.70	-	-	53.01	-	-
5.	[(μ-Cl)₂Al₂(η²-osmab)₂]	152.81	153.63	150.80,124.69, 123.70	-	-	-	-	-
6.	[(μ-OAl)₂ Al₂(η²-ovmab)₂]	153.31	158.68	132.50,125.67, 122.70	-	-	54.02	-	-
7.	[(μ-OAl)₂ Al₂(η²-osmab)₂]	154.69	157.02	145.60,126.79, 121.30,	-	-	-	-	-
8.	[(η¹-osmab)₂Al[μ-OPrⁱ]₂{Al(OPrⁱ)₂}]	153.79	159.21	143.20,121.80, 121.97	-	-		60.69	63.89
9.	[(η¹-ovmab)₂Al[μ-OPrⁱ]₂{Al(OPrⁱ)₂}]	156.69	157.03	143.40,125.47, 120.60	-	-	53.04	61.70	64.79
10.	[(η¹-ovas)Al(η²-osab)(η¹-osab)]	158.89	160.02	139.10,125.90, 121.70	168.58	178.69	-	-	-

Table -15

^{13}C Nuclear magnetic resonance (NMR) spectral data of Aluminium(III) complexes containing Schiff bases

Sl. No.	Compound	-OH	Azomethine CH=N	Aromatic carbon	-COOH	OCH₃	Amido carbon	Isopropoxide	
								Terminal	Bridging
1.	[(μ-Cl)₂Al₂ (CH₃)(η²-osmalb)₂]	152.02	153.30	138.34,124.69,119.60	-	-	-	-	-
2.	[(μ-Cl)₂Al₂ (CH₃)(η²-ovmalb)₂]	158.05	154.40	148.39,123.47,121.70	-	53.06	-	-	-
3.	[(μ-Cl)₂Al₂ (η²-osmalb)₂]	161.20	160.03	144.20,122.20,120.79	-	-	-	-	-
4.	[(μ-Cl)₂Al₂(η²-ovmalb)₂]	160.28	157.03	146.60,126.79,121.30	-	54.02	-	-	-
5.	[(μ-OAr)₂Al₂(η²-osmalb)₂]	156.14	159.02	138.50,126.79,121.30	-	-	-	-	-
6.	[(μ-OAr)₂ Al₂(η²-ovalb)₂]	155.69	158.68	150.10,125.59,121.21	-	53.06	-	-	-
7.	[(η²-osmalb)₂Al[μ-OPⁱ⁻]₂[Al(OPⁱ⁻)₂]]	157.89	157.81	143.80,126.19,121.90	-	-	-	61.79	64.80
8.	[(η²-ovalb)₂Al[μ-OPⁱ⁻]₂[Al(OPⁱ⁻)₂]]	158.63	156.68	147.60,124.80,123.70	-	53.04	-	60.69	63.84
9.	[(η²-osmair)Al(η²-osalr)(η²-oialb)]	154.54	157.68	137.40,123.60,121.60	-	-	158.76	-	-
10.	[(η²-osas)₂Al(η²-osts)(η²-oialb)]	161.20	158.60	138.20,125.40,122.60	167.68	-	166.02	-	-

2.2.4.5 FAB-mass Spectral Studies

The FAB-mass spectral investigation was performed, for the representative complexes containing various Schiff bases as well as some mixed ligand complexes synthesised during present course of investigation. Molecular ion peak along with some characteristic peaks were observed for their complexes, which convincingly support the composition of these interesting new complexes [143-144].

The FAB-mass spectral studies of dichloro Aluminium (III) complexes such as $[(\mu\text{-Cl})_2Al_2(Cl_2)(\eta^2\text{-ovmab})_2]$ showed characteristic molecular ion $[M^+]$ peak at m/z = 676. Which correspond to the molecular weight of the compound, another peak obtained at m/z =338 indicated the fragmentation of dimer to monomer. Beside these other fragmentation peak obtained indicating the fragmentation of ligand from monomer by the formation of radical cation.

The characteristic fragmentation ion peak of complexes are summarized in Scheme (4.1).

$$[C_{30}H_{28}N_2O_4Cl_4Al_2] \xrightarrow[\text{-2e}]{+ e^-} [C_{30}H_{28}N_2O_4Cl_4Al_2]^+$$

m/z = 676(dimer)

$$[C_{15}H_{14}NO_2AlCl_2]^{\dot{+}}$$
m/z = 338.31 (monomer)

$\downarrow$ - $C_7H_7^{\cdot}$

$$[C_8H_7NO_2AlCl_2]^+$$
m/z = 247

$\downarrow$ - $OCH_3^{\cdot}$

$[AlCl]^+$ $[C_7H_4NOAlCl_2]^{\dot{+}}$
m/z = 62   m/z = 247

$\uparrow$ - $Cl^{\cdot}$ $\downarrow$ - $HCN^{\cdot}$

$[AlCl_2]^{\cdot+}$ $\xleftarrow{- OC_6H_3^{\cdot}}$ $[C_6H_3OAlCl_2]^+$ $\xleftarrow{- HCN}$ $[C_7H_4NOAlCl_2]^{\dot{+}}$
m/z = 98.3   m/z = 189   m/z = 247
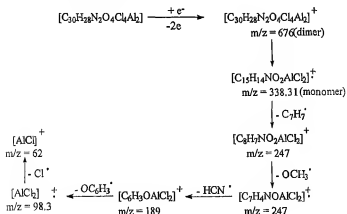
Scheme-4.1 **FAB-mass** **Fragmentation** **Pattern** of $[(\mu\text{-Cl})_2Al_2(Al)\{\eta^2\text{-(ovmab)}\}_4]$

The FAB-mass spectral studies of monochloro Aluminium (III) complexes $[(\mu\text{-Cl})_2Al_2(\eta^2\text{-osnab})_4]$ showed characteristic molecular ion peak at m/z = 1089 which correspond to molecular weight of compound; another peak obtained at m/z = 544 confirms fragmentation of dimer to monomer besides these other peak may be obtained due to fragmentation of ligand moiety from monomer.

Characteristic fragmentation ion peaks are summarized in Scheme 4.2.

$$[C_{52}H_{36}N_8O_{12}Al_2Cl_2] \xrightarrow[-2e]{+e} [C_{52}H_{36}N_8O_{12}Al_2Cl_2]^+$$

$$m/z = 1089 \text{ (dimer)}$$

$$\downarrow$$

$$[C_{26}H_{18}N_4O_6AlCl]^+$$
$$m/z = 544 \text{ (monomer)}$$

$$\downarrow -C_6H_4NO_2^{\cdot}$$

$$[C_{20}H_{14}N_3O_4AlCl]^+$$
$$m/z = 422$$

$$\downarrow -C_6H_4NO_2^{\cdot}$$

$$[AlCl]^+ \qquad\qquad [C_{14}H_{10}N_2O_2AlCl]^+$$
$$m/z = 62 \qquad\qquad m/z = 300$$

$$\uparrow -C_6H_4O^{\cdot}$$

$$[C_6H_4OAlCl]^+ \xleftarrow{-C_6H_5O^{\cdot}} [C_{13}H_9O_2AlCl]^+ \xleftarrow{-HCN^{\cdot}}$$
$$m/z = 154 \qquad\qquad m/z = 246$$
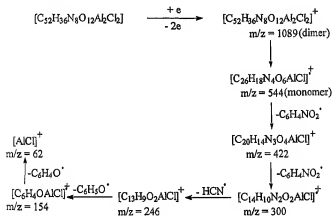
Scheme-4.2   FAB-mass   Fragmentation   Pattern   of
$$[(\mu\text{-Cl})_2Al_2\{\eta^2\text{-(osnab)}\}_4]$$
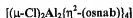
The FAB-mass spectral studies of mixed ligand complexes $[(\mu\text{-Cl})_2Al_2(\eta^2\text{-osnab})_4]$ showed characteristic molecular ion $[M^+]$ peak at m/z = 684 which correspond to molecular weight of compound, suggest monomeric nature of complex. The fragmentation of the complex represented by scheme 4.3.

$[C_{42}H_{34}N_4O_4Al]$ $\xrightarrow[-2e^-]{+e}$ $[C_{42}H_{34}N_4O_4Al]^+$ $\xrightarrow{-C_7H_7^{\bullet}}$ $[C_{29}H_{28}N_4O_4Al]^{+}$
m/z = 684   m/z = 518

↓ -OCH$_3^{\bullet}$

$[C_{28}H_{21}N_4O_3Al]^+$
m/z = 487

↓ - C$_6$H$_4$O$^{\bullet}$

$[C_{22}H_{17}N_4O_2Al]^{+}$
m/z = 395

↓ -HCN$^{\bullet}$

$[Al]^+$
m/z = 27

↓ - HCN$^{\bullet}$

$[CHNOAl]^{+}$
m/z = 53

↓ - C$_3$H$_7$O$^{\bullet}$

$[C_7H_8NOAl]^+$
m/z = 147

↓ - NCO$^{\bullet}$

$[C_{21}H_{16}N_3O_2Al]^{+}$
m/z = 368

↓ -C$_7$H$_4^{\bullet}$

$[C_{13}H_{12}N_3O_2Al]^{+}$
m/z = 291

$[C_8H_8N_2O_2Al]^{+}$ $\xleftarrow{- CN^{\bullet}}$ $[C_9H_8N_3O_2Al]^+$ $\xleftarrow{- C_6H_4^{\bullet}}$
m/z = 189   m/z = 215
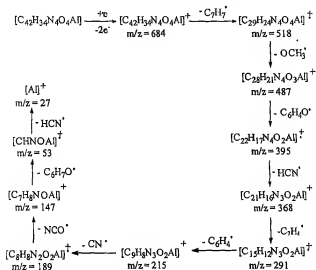
Scheme-4.3 FAB-mass Fragmentation Pattern of mixed ligand complexes $[(\eta^2\text{-ovmab})Al(\eta^2\text{-osab})(\eta^2\text{-oiab})]$

Chapter-III

RESULTS

&

DISCUSSION

Synthesis, Reactions and Physico-chemical
Studies of Antimony (III) Complexes
Containing Various Schiff Bases

3.1 INTRODUCTION

The first Antimony trichloride adduct with neutral ligand was reported in 1910 [145], then the adduct forming tendency of salicylideneanilines towards various transition and non transition metal halides has been investigated [146-150]. The Schiff base complexes of main group as well as transition metals with Schiff base ligands containing sulphur and nitrogen as a donor atom have been extensively studied owing to their antitumor, antimalarial and antibacterial activities [151-155].

The use of Antimony in medicine have been reviewed by Tiekink [148] over last several year. Silvestru & Coworkers [156-159] showed that some organoantimony (III) derivatives showed significant antitumour activity [160-165]. However, dimethyl canthramide and its analogues have also showed a wide range of biological activity.

The vanillidene-2-methyl-1-amino benzene (vmabH), salicylidene-3-nitro-1-aminobenzene(snabH), vanillidene-1-aminobenzene (vabH), salicylidene-anthranilic acid (saaH), vanillidene-anthranilic acid (vaaH), 4-nitrobenzylidene-2-aminophenol (nbaphH), isatidene-3-nitro-1-aminobenzene (inabpH), salicylidene-1-aminobenzene (sabH) and isatidene-1-aminobenzene (iabH) have been utilized to produce new hydrocarbon soluble mixed ligand complexes however other aspect of coordination chemistry of Schiff bases such as −

(i)   Preparation of monochloro Schiff base complexes and their chemical reactions with various ligands to produce hydrocarbon soluble mixed ligand complexes.

(ii) Preparation of hydrocarbon soluble bimetallic mixed ligand complexes have not been explored so far.

Synthesis of hydrocarbon soluble Schiff base complexes of main group metal complexes containing alkoxo-, phenoxo-, ligands have received only scant attention. It is of great interest to explore the chemistry and bonding characteristics to throw light towards coordination behaviour and structural aspects of various phenoxo bridged (binuclear), mixed ligand and alkoxo bridged (bimetallic) Schiff base metal complexes of Antimony (III).

Therefore we report here in the synthesis, reaction and physico-chemical studies of Antimony (III) complexes containing various Schiff bases of the type $[(Cl)_2Sb(SB)]$, $[(Cl)Sb(SB)_2]$ and $[(SB)Sb(S'B') \ (S''B'')]$ [where S.B. = Schiff base such as (vmabH, snabH, smabH, vabH, nbaphH, vaaH, saaH and iabH, $S'B'$ = iabH, $S''B''$ = sabH.] The structural determination of complexes have been carried out by Infrared, Electronic (^{1}H and C^{13}) NMR, and FAB-mass spectral studies.

3.2   Results and Discussion

3.3.1 Synthesis and physico-chemical studies of Antimony (III) complexes of the types [(Cl)₂Sb(η²-ovmab)], [(Cl)₂Sb(η²-osnab)], [(Cl)Sb(η²-ovmab)₂] and [(Cl)Sb(η²-osnab)₂].

Antimony (III) complexes containing Schiff bases have been prepared by the reactions of anhydrous Antimony (III) chloride with sodium salt of vanillidene-2-methyl-1-aminobenzene (vmabH) and salicylidene-3-nitro-1-aminobenzene (snabH) in 1:1 and 1:2 molar ratios in dry benzene-methanol mixture, afforded complexes of the type [(Cl)₂Sb(η²-ovmab)], [(Cl)₂Sb(η²-osnab)], [(Cl)Sb(η²-ovmab)₂] and [(Cl)Sb(η²-osnab)₂] which can be illustrated by the following chemical equations.
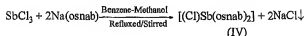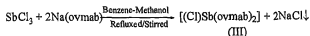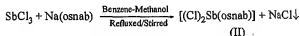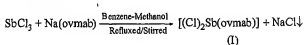
$$SbCl_3 + Na(ovmab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)_2Sb(ovmab)] + NaCl\downarrow$$
$$(I)$$

$$SbCl_3 + Na(osnab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)_2Sb(osnab)] + NaCl\downarrow$$
$$(II)$$

$$SbCl_3 + 2Na(ovmab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)Sb(ovmab)_2] + 2NaCl\downarrow$$
$$(III)$$

$$SbCl_3 + 2Na(osnab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)Sb(osnab)_2] + 2NaCl\downarrow$$
$$(IV)$$

The above complexes are coloured solid and are soluble in common organic solvents such as methanol, CCl_4, $CHCl_3$, DMSO,

DMF, and purified by recrystallisation in benzene-methanol mixture. Some physical properties are listed in Table [16-17].

3.2.1.1 Reactions of [(Cl)Sb(η^2-ovmab)$_2$] and [(Cl)Sb(η^2-osnab)$_2$]

(i) *With sodium phenolate [Na(OAr)]*

The reaction of monochloro Antimony (III) complexes [(Cl)Sb(η^2-ovmab)] and [(Cl)Sb(η^2-osnab)] with sodium salt of 4-nitrophenol in equimolar ratio in benzene-methanol mixture produced complexes of the type [(μ-OAr)Sb(η^2-ovmab)], and [(μ-OAr)Sb(η^2-osnab)$_2$] which can be represented by the following chemical equations,

$$[(Cl)Sb(ovmab)_2] + Na(OAr) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(ovmab)_2Sb(OAr)] + NaCl,$$
$$(IIIa)$$

$$[(Cl)Sb(osnab)_2] + Na(OAr) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(osnab)_2Sb(OAr)] + NaCl\downarrow$$
$$(IVa)$$

These complexes are coloured solids and are soluble in common organic solvents. All these complexes have been purified by recrystallisation in benzene-methanol mixture. The physical properties of these complexes are listed in Table [16-17].

(ii) *With sodium tetralkoxyaluminate [Na{Al(OPi)$_4$}]*

The reaction of monochloro Antimony (III) complexes such as [(Cl)Sb(η^2-ovmab)$_2$] and [(Cl)Sb(η^2-osnab)$_2$] containing Schiff bases

with sodium salt of tetraisopropoxyaluminate $[Na\{Al(OPr^i)_4\}]$ in 1:1 stoichiometric ratio in benzene methanol mixture produces bimetallic complexes of the type $[(\eta^2\text{-ovmab})_2Sb\{Al(OPr^i)_4\}]$ and $[(\eta^2\text{-osnab})_2Sb\{Al(OPr^i)_4\}]$ which can be demonstrated as follows.

$$[(Cl)Sb(ovmab)_2] + Na\{Al(OPr^i)_4\} \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(ovmab)_2Sb\{Al(OPr^i)_4\}] + NaCl\downarrow$$
$$\text{(IIIb)}$$

$$[(Cl)Sb(osnab)_2] + Na\{Al(OPr^i)_4\} \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(osnab)_2Sb\{Al(OPr^i)_4\}] + NaCl\downarrow$$
$$\text{(IVb)}$$

These bimetallic complexes are light brown crystalline solids and are fairly soluble in common organic solvents such as (methanol, benzene CHCl₃ THF, DMF, DMSO) and purified by benzene methanol mixture physical properties are given in Table [16-17].

3.2.2 Synthesis and physico-chemical studies of Antimony(III) complexes of the types $[(Cl)_2Sb(\eta^2\text{-osmab})]$, $[(Cl)_2Sb(\eta^2\text{-ovab})]$, $[(Cl)Sb(\eta^2\text{-osmab})_2]$ and $[(Cl)Sb(\eta^2\text{-ovab})_2]$.

When a hot solution of anhydrous SbCl₃ in benzene was added slowly to the freshly prepared sodium salt of salicyllidene-2-methyl aminobenzene(smabH) and vanillidene-1-aminobenzene (vabH) in benzene methanol mixture in 1:1 and 1:2 molar ratio afforded complexes of the types $[(Cl)_2Sb(\eta^2\text{-osmab})]$, $[(Cl)_2Sb(\eta^2\text{-ovab})]$, $[(Cl)Sb(\eta^2\text{-osmab})_2]$ and $[(Cl)Sb(\eta^2\text{-ovab})_2]$ which can be represented by the following chemical equations :
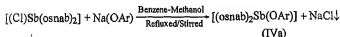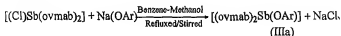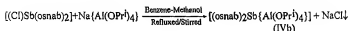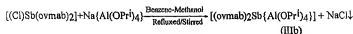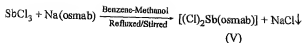
$$SbCl_3 + Na(osmab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)_2Sb(osmab)] + NaCl\downarrow$$
$$(V)$$

$$SbCl_3 + Na(ovab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)_2Sb(ovab)] + NaCl\downarrow$$
$$(VI)$$

$$SbCl_3 + 2Na(osmab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)Sb(osmab)_2] + 2NaCl\downarrow$$
$$(VII)$$

$$SbCl_3 + 2Na(ovab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)Sb(ovab)_2] + 2NaCl\downarrow$$
$$(VIII)$$

These freshly prepared complexes are found to be coloured solid, soluble in common organic solvents such as methanol, CHCl$_3$, THF, DMSO, and are partially soluble in benzene. All these complexes have been purified by recrystallisation in benzene-methanol mixture. Some of their physical properties are given in Table [16-17].

3.3.2.1 Reaction of [(Cl)Sb(η²-osmab)₂], [(Cl)Sb(η²-ovab)₂].

(i) With sodium phenolate [Na(OAr)] :

The chlorine replacement reactions of monochloro Antimony (III) complexes such as [(Cl)Sb(η²-osmab)₂] and [(Cl)Sb(η²-ovab)₂], with sodium salt of 4-nitrophenol in 1:1 stoichiometric ratio in benzene-methonal, mixture produces complexes of the type [(μ-OAr)Sb(η²-osmab)₂] and [(μ-OAr)Sb(η²-ovab)₂] which have been demonstrated by the following chemical equations.

$$[(Cl)Sb(osmab)_2] + Na(OAr) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(OAr)Sb(osmab)_2] + NaCl\downarrow$$
$$(VIIa)$$

$$[(Cl)Sb(ovab)_2] + Na(OAr) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(OAr)Sb(ovab)_2] + NaCl\downarrow$$
$$(VIIIa)$$
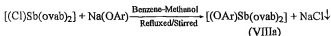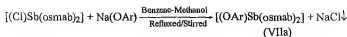
These complexes are coloured solids, soluble in common organic solvents like benzene, alcohol, THF and purified by recrystallization in solution of benzene methanol mixture. Details of their physical properties are listed in Table [16-17].

(ii) *With sodium tetraisopropoxyaluminate [Na(Al(OPr^i)$_4$]*

The chloride replacement reactions of monochloro Antimony (III) complexes are $[(Cl)Sb(\eta^2\text{-osmab})_2]$ and $[(Cl)Sb(\eta^2\text{-ovab})_2]$, have been carried out with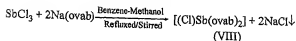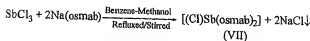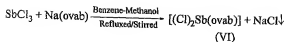 sodium salt of tetraisopropoxyaluminate $[Na\{Al(OPr^i)_4\}]$ in 1:1 molar ratio in the presence of benzene-methanol, mixture to produce alkoxo-bridged (bimetallic) complexes of the type $[(\eta^2\text{-osmab})_2Sb\{Al(OPr^i)_4\}]$ and $[(\eta^2\text{-ovab})_2Sb\{Al(OPr^i)_4\}]$ which can be shown by following chemical equations.

$$[(Cl)Sb(osmab)_2] + Na\{Al(OPr^i)_4\} \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(osmab)_2Sb\{Al(OPr^i)_4\}] + NaCl\downarrow$$
$$(VIIb)$$

$$[(Cl)Sb(ovab)_2] + Na\{Al(OPr^i)_4\} \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(ovab)_2Sb\{Al(OPr^i)_4\}] + NaCl\downarrow$$
$$(VIIIb)$$
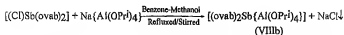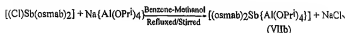
These bimetallic complexes are coloured solid and fairly soluble in benzene, n-hexane, THF and purified by recrystallisation in methanol benzene mixture.

3.3.3 Synthesis and Physico-chemical Studies of mixed ligand complexes of Antimony (III) of the type [(SB)Sb(S'B')(S"B")].

The mixed ligand complexes of the type [(SB)Sb(S'B')(S"B")] have been prepared by interactions of freshly prepared dichloro [(Cl₂)Sb(SB)] complexess of Antimony (III) with sodium salt of ligand Na(S'B') and Na(S"B") in 1:1:1 molar ratio in benzene-methanol mixture {where SB=vmabH, snabH, vabH, saaH, vaaH, inabH, nbaphH, S'B'=iabH and S"B"=sabH} complexes represented by following chemical equation.

$[(Cl)_2Sb(ovmab)] + Na(oiab)+Na(osab) \xrightarrow{\text{Benzene-Methanol}}_{\text{Refluxed/Stirred}} [(ovmab)Sb(oiab)(osab)] + 2NaCl\downarrow$

(IX)

$[(Cl)_2Sb(osnab)] + Na(oiab)+Na(osab) \xrightarrow{\text{Benzene-Methanol}}_{\text{Refluxed/Stirred}} [(osnab)Sb(oiab)(osab)] + 2NaCl\downarrow$

(X)

$[(Cl)_2Sb(osmab)] + Na(oiab)+Na(osab) \xrightarrow{\text{Benzene-Methanol}}_{\text{Refluxed/Stirred}} [(osmab)Sb(oiab)(osab)] + 2NaCl\downarrow$

(XI)

$[(Cl)_2Sb(ovab)] + Na(oiab)+Na(osab) \xrightarrow{\text{Benzene-Methanol}}_{\text{Refluxed/Stirred}} [(ovab)Sb(oiab)(osab)] + 2NaCl\downarrow$

(XII)

$[(Cl)_2Sb(osaa)] + Na(oiab)+Na(osab) \xrightarrow{\text{Benzene-Methanol}}_{\text{Refluxed/Stirred}} [(osaa)Sb(oiab)(osab)] + 2NaCl\downarrow$

(XIII)

$[(Cl)_2Sb(ovaa)] + Na(oiab)+Na(osab) \xrightarrow{\text{Benzene-Methanol}}_{\text{Refluxed/Stirred}} [(ovaa)Sb(oiab)(osab)] + 2NaCl\downarrow$

(XIV)

$$[(Cl)_2Sb(oinab)] + Na(oiab) + Na(osab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(oinab)Sb(oiab)(osab)] + 2NaCl\downarrow$$
$$(XV)$$

$$[(Cl)_2Sb(onbaph)] + Na(oiab) + Na(osab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(onbaph)Sb(oiab)(osab)] + 2NaCl\downarrow$$
$$(XVI)$$

These mixed ligand complexes are coloured solids, soluble in common organic solvents and are purified by recrystallisation in benzene-methanol, mixture some of their physical properties are collected in Table [16-17],

Table-16

Physical properties of Antimony (III) complexes containing Schiff bases

Sl. No.	Complexes	Physical State	m.p. (°C)
1.	$[(Cl)_2Sb(\eta^2\text{-ovmab})]$	Dark yellow solid	140
2.	$[(Cl)_2Sb(\eta^2\text{-osnab})]$	Brown solid	125
3.	$[(Cl)Sb(\eta^2\text{-ovmab})_2]$	Dark yellow solid	132
4.	$[(Cl)Sb(\eta^2\text{-onab})_2]$	Dark yellow	148
5.	$[(OAr)Sb(\eta^2\text{-ovmab})_2]$	Cream colour solid	152
6.	$[(OAr)Sb(\eta^2\text{-osnab})_2]$	Yellowish green solid	187
7.	$[(\eta^2\text{-ovmab})_2Sb(\mu\text{-OPr}^i)_2\{Al(OPr^i)_2\}]$	Brown coloured solid	298[a]
8.	$[(\eta^2\text{-osnab})_2Sb(\mu\text{-OPr}^i)_2\{Al(OPr^i)_2\}]$	Light brown solid	288[a]
9.	$[(\eta^2\text{-ovmab})Sb(\eta^2\text{-osab})(\eta^2\text{-oiab})]$	Pink coloured solid	167
10.	$[(\eta^2\text{-osnab})Sb(\eta^2\text{-osab})(\eta^2\text{-oiab})]$	Light yellow	175
11.	$[(\eta^2\text{-osmab})Sb(\eta^2\text{-oseb})(\eta^2\text{-oiab})]$	Dirty brown solid	163
12.	$[(\eta^2\text{-ovab})Sb(\eta^2\text{-osab})(\eta^2\text{-oiab})]$	Dark yellow solid .	170

a = neither melt nor decomposed.

Table -17

Physical properties of Antimony (III) complexes containing Schiff bases

Sl. No.	Complexes	Physical State	m.p. (°C)
1.	$[(Cl)_2Sb(\eta^2\text{-osmab})]$	Light yellow	143
2.	$[(Cl)_2Sb(\eta^2\text{-ovab})]$	Brownish yellow solid	170
3.	$[(Cl)Sb(\eta^2\text{-osmab})_2]$	Light brown solid	158
4.	$[(Cl)Sb(\eta^2\text{-ovab})_2]$	Reddish yellow	176
5.	$[(OAr)Sb(\eta^2\text{-osmab})_2]$	Greenyallow solid	210
6.	$[(OAr)Sb(\eta^2\text{-ovab})_2]$	Brownish brown solid	227
7.	$[(\eta^2\text{-osmab})Sb(\mu\text{-OPr}^i)_2 \{Al_2(OPr^i)_2\}]$	Whitish yellow solid	287[a]
8.	$[(\eta^2\text{-ovab})_2Sb(\mu\text{-OPr}^i)_2\{Al(OPr^i)_2\}]$	Light yellow solid	298[a]
9.	$[(\eta^2\text{-osaa})Sb(\eta^2\text{-osab})(\eta^2\text{-oiab})]$	Pinkish yellow solid	221
10.	$[(\eta^2\text{-ovaa})Sb(\eta^2\text{-osab})(\eta^2\text{-ovab})]$	Light brown solid	213
11.	$[(\eta^2\text{-oinlb})Sb(\eta^2\text{-osab})(\eta^2\text{-oiab})]$	Red coloured solid	168
12.	$[(\eta^2\text{-onbaph})Sb(\eta^2\text{-osab})(\eta^2\text{-oiab})]$	Brownish solid	238

a = neither melt nor decomposed.

3.3.4 Spectral Studies of Antimony (III) Complexes Containing Schiff bases.

Infrared, Electronic (U.V.-visible) FAB-mass and Nuclear Magnetic Resonance (^{1}H & ^{13}C) spectra have been recorded for Antimony (III) complexes in order to understand the coordination behaviour around Antimony(III). The important conclusion drawn from these analytical techniques are furnished below systematically which in turn have been utilised in predicting structural features of complexes under study.

3.3.4.1 Infrared Spectral Studies

Infrared spectra of Antimony (III) complexes containing Schiff bases such as vanillidene-2-methyl-1-amino benzene (vmabH) salicylidene-3-nitro-1-aminobenzene(snabH), vanillidene-1-aminobenzene (vabH), salicylidene-anthranilic ·acid (saaH), vanillidene-anthranilic acid (vaaH), 4-nitrobenzylidene-2-aminophenol (nbaphH), isatidene-3-nitro-1-aminobenzene (inabpH), salicylidene-1-aminobenzene (sabH) and isatidene-1-aminobenzene (iabH). The characteristic features of their infrared spectra are the appearance of band for v_{Sb-Cl} (348-352) cm^{-1}, v_{Sb-N}(540-580)cm^{-1}, v_{Sb-O}(425-440)cm^{-1}.

The presence of Schiff base moieties indicated by the appearance of absorption band at 1648-1618 cm^{-1} in ligands is characteristic for $v_{C=N}$ in the complexes shifted of $v_{C=N}$ band to lower

wave number at 1622-1595 cm^{-1} , [166-169] indicates coordination of azomethine nitrogen with metal ion.

The Schiff bases generally (containing phenolic group) displays two IR bands at ~3564-3329 cm^{-1} and at 1389-1310 cm^{-1}, which have been specified for v_{OH} stretching and v_{OH} deformation frequencies respectively. These frequencies disappeared in the spectra of Antimony (III) complexes suggesting deprotonation of phenolic OH after chelating with [170-175] metal ion.

The $v_{(C-O)}$ phenolic band were observed at 1277-1266 cm^{-1} in all the Schiff bases. These bands shifted to higher wave number (1293-1270) cm^{-1} suggesting coordination [176-177] through phenolic oxygen.

The dichloro and monochloro complexes [(Cl)$_2$Sb(η^2-ovmab)](I), [(Cl)$_2$Sb(η^2-osnab)](II), [(Cl)Sb(ovmab)$_2$] (III), [(Cl)Sb(η^2-osnab)$_2$](IV), [(Cl)$_2$Sb(η^2-osmab)](V), [(Cl)$_2$Sb(η^2-ovab)](VI), [(Cl)$_2$Sb(η^2-osmab)$_2$](VII) and [(Cl)Sb(η^2-ovab)$_2$](VIII) displays sharp IR bands in the region 350-335 cm^{-1} assigned for $v_{(Sb-Cl)}$ metal-chlorine stretching frequency [178-181] on the basis of above findings. The following representative structure have been suggested.
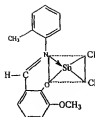
Fig. 24 Proposed Structure of [(Cl)₂Sb(η²-ovmab)]

The infrared spectra of phenoxo containing, complexes
[(η²-ovmab)₂Sb(μ-OAr)] (IIIa), [(μ-OAr)Sb(η²-osnab)] (IVa),
[(μ-OAr)Sb(η²-osmab)₂] (VIIa) and [(μ-OAr)Sb(η²-ovab)₂] (VIIIa),
the $v_{(C-O)}$ frequency of free ligand obtained at 1272-1266 cm⁻¹ this
band shifted (11-21) cm⁻¹ higher in complexes assigned to
C-O(phenolic) group stretching suggesting that bonding may occurs
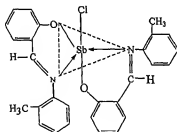
Fig. 25 Proposed Structure of [(Cl)₂Sb(η²-osmab)]

through phenolic oxygen. On the basis of above findings following
structure may be proposed.
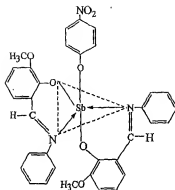
Fig. 26 Proposed Structure for [(OAr) Sb(η^2-ovab)$_2$]

The infrared spectra of alkoxo-bridged complexes [(η^2-ovnab)$_2$Sb(μ-OPri){Al(OPri)$_2$}] (IIIb), [(η^2-osnab)$_2$Sb OPri){Al(OPri)$_2$}] (IVb), [(η^2-osmab)$_2$Sb (μ-OPr^i)$_2${Al(OPri)$_2$}](VIIb) and [(η^2-ovab)$_2$Sb(μ-OPr^i)$_2$ {Al(μ-OPr^i)$_2$}](VIIIb) showed characteristic strong intensity band in the region 1025-1015 cm^{-1} which may be specified for $v_{(C-O)}$ terminal alkoxy group and for bridging alkoxy group at about 751-735 cm^{-1}. On the basis of above finding following structure [182-190] have been suggested.
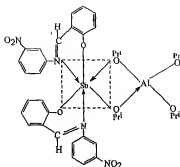
Fig. 27 Proposed Structure for [(osnab)$_2$Sb (μ-OPri){Al(OPri)$_2$}]

In the infrared spectra of the complexes some additional bands have been obtained which were not present in the spectra of ligand, but observed in corresponding Antimony (III) complexes. A new band present in the region 440-425 cm^{-1} may be attributed to the $v_{(Sb-O)}$ stretching vibration. This vibration shifted (20cm^{-1}) higher in chloro (monochloro & dichloro) [191] complexes in comparison to mixed ligand complexes.

In the complexes [192-196] bands appeared at 580-540 cm^{-1} are assigned to $v_{(Sb-N)}$ vibrations. This data suggested the possible trans configuration for two ligand molecules around Antimony(III). However a band found at approximately 530 cm^{-1} which characterizes cis environment of ligand around metal. Table[18-19].

Table-18

Characteristic IR frequencies (cm^{-1}) of Antimony(III) complexes containing Schiff bases

Sl. No.	Complexes	ν_{Sb-Cl}	ν_{Sb-N}	ν_{Sb-O}	ν_{C-O} Phenolic	$\nu_{C=N}$	ν_{C-O} Alkoxy	ν_{Al-O}
1.	[(η²-ovmab)Sb (Cl)₂]	350	570	438	1282	1608	-	-
2.	[(η²-osnab)Sb (Cl)₂]	335	578	440	1283	1609	-	-
3.	[(η²-ovmab)₂Sb (Cl)]	340	580	438	1284	1611	-	-
4.	[(η²-osnab)₂Sb (Cl)]	345	546	439	1286	1607	-	-
5.	[(η²-ovmab)₂Sb (OAr)]		450	430	1291	1610	-	-
6.	[(η²-osnab)₂Sb (OAr)]		575	432	1289	1613	-	-
7.	[(η²-ovmab)₂Sb(μ-OPh)₂{Al(OPh)₃}]		568	430	1280	1611	1127ᵈ 966ᵇ	620
8.	[(η²-osnab)₂Sb(μ-OPh)₂{Al(OPh)₃}]		572	428	1290	1605	1140ᵈ 948ᵇ	600
9.	[(η²-ovmab)Sb (η²-osab) (η¹-olab)]		573	426	1288	1608		
10.	[(η²-osnab)Sb (η²-osab) (η¹-olab)]		545	428	1285	1613		
11.	[(η²-osnab)Sb (η²-osab) (η¹-olab)]		450	427	1283	1617		
12.	[(η²-ovab)Sb(η²-osab) (η¹-olab)]		540	426	1289	1602		

t=terminal , b=bridging

Table-19

Characteristic IR Frequencies (cm⁻¹) of Antimony(III) complexes containing Schiff bases

Sl. No.	Complexes	νSb-Cl	νSb-N	νSb-O	νC-O Phenolic	νC=N	νC-OSb Alkoxy	νSb-O
1.	[(Cl)₂Sb(η¹-osnab)]	350	580	442	1285	1617	-	-
2.	[(Cl)₂Sb(η¹-ovab)]	348	545	443	1284	1610	-	-
3.	[(Cl)Sb(η¹-osnab)₂]	352	560	440	1285	1615	-	-
4.	[(Cl)Sb(η¹-ovab)₂]	351	570	439	1283	1611	"	-
5.	[(OAc)₂Sb(η¹-osnab)]		578	420	1290	1611	-	-
6.	[(OAc)₂Sb(η¹-ovab)]		581	415	1283	1609	-	-
7.	[(η¹-osnab)₂Sb(μ-OPⁱ₂)₂{Al(OPⁱ₂)₃}]		579	420	1281	1613	1150ᵇ 950ᵇ	630
8.	[(η¹-ovab)₂Sb(μ-OPⁱ₂)₂{Al(OPⁱ₂)₃}]		585	422	1282	1607	1140ᵇ 948ᵇ	625
9.	[(η¹-osna)Sb(η¹-osab)(η¹-olab)]		549	433	1286	1612		
10.	[(η¹-ovap)Sb(η¹-osab)(η¹-olab)]		560	428	1281	1603		
11.	[(η¹-olnab)Sb(η¹-osab)(η¹-olab)]		580	427	1285	1607		
12.	[(η¹-onbaph)Sb(η¹-osab)(η¹-olab)]		561	430	1280	1609		

t=terminal, b= bridging, isopropoxy group

3.3.4.2 Electronic Spectral Studies

The electronic spectra of Schiff base [170] Antimony(III) complexes, exhibited three bands around 44802, 37202 and 29620 possibly due to π–π* transition of benzenoid ring in conjugation with double bond of azomethine group. The band around 25000 cm^{-1} may be due to n–π* transition of bonding electron present in the nitrogen of azomethine group in the corresponding Antimony(III) complexes. There is no shift in the position of first two bands. These bands in the complexes are slightly broader in nature due to presence of two different type of Schiff bases in the complexes. The ligand bands showed bathochromic shift in the complexes may be due to coordination of azomethine nitrogen with central Antimony(III) atom Table [20].

Table – 20

Electronic (U.V.–visible) spectral data of Antimony (III) complexes containing Schiff bases

Sl. No.	Complexes	Transitions (cm^{-1})	
		$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
1.	[(η²-ovmab)₂ Sb(Cl)₃]	25000	44802
2.	[(η²-osmab)₂ Sb(Cl)₃]	25600	43742
3.	[(η²-ovmab)₂ Sb(Cl)]	25700	37202
4.	[(η²-osmab)₂ Sb(Cl)]	25320	29620
5.	[(η²-ovmab)₂ Sb(OAc)]	25128	30440
6.	[(η²-osmab)₂ Sb(OAc)]	25345	34865
7.	[(η²-osmab)₂ Sb(μ–OPⁿPr₂)₂[Al(OPⁿPr)₄]	25242	43807
8.	[(η²-ovmab)₂ Sb(μ–OPⁿPr₂)₂[Al(OPⁿPr)₄]	25110	42802
9.	[(η²-ovmab)Sb(η²-osab) (η²-oiab)]	25610	40342
10.	[(η²-osmab)Sb(η²-osab) (η²-oiab)]	25398	38342

3.3.4.3 Proton Magnetic Resonance Spectroscopy

The proton magnetic resonance spectra of these complexes recorded in deutrated chloroform and in DMSO-d_6. The spectra are quite complicated due to homo and hetero nuclear spin-spin coupling, so it is not easy to interpret, however, a comparison of the spectra of ligand with that of the complexes can lead to the following conclusions Table [21,22].

(i). A strong signal appeared in the [135] region δ13.6-13.8 ppm may be assigned to OH proton of Schiff bases however, this signal disappeared in the spectra of corresponding Antimony(III) complexes, indicating the deprotonation of OH and Sb-O bond formation may occurs.

(ii). The proton signal appeared in the [136] region δ8.10 ppm in free ligand due to azomethine proton. This signal shifted down field in Antimony (III) complexes from δ8.10 to 9.25 ppm suggesting. That azomethine nitrogen involved in coordination with Antimony (III).

(iii). The chemical shift due to aromatic ring protons appeared at δ7.8-8.4 ppm in ligands, which may be shifted slightly down field in the complexes may be due to decrease in electron density after formation of complex.

(iv). All these complexes containing vanillidene Schiff base showed an [135] (I, III, IIIa, IIIb, IV, VII, VIIIa, VIIIb, IX, XII, XIV) extra proton signal due to m-OCH₃ group at about δ3.50-3.90 ppm.

(v) A singlet due to NH obtained [137] at δ11.2 ppm in the spectra of isatin derived ligands which may be disappeared in the complexes (IX, X, XI, XII, XIII, XIV, XV, XVI) further indicating enolization of keto group and coordination may occur through oxygen.

(vi) The methine proton of terminal [138] and bridging isopropoxy groups are observed at δ3.90-399 and δ4.06-4.25 ppm respectively. The data may suggests that Antimony (III) bonded (IIIb, VIb, VIIb, VIIIb) with tetraalkoxyaluminate through isopropoxy bridged structure.

The signal due to other protons in Schiff bases and their shift in their corresponding Antimony (III) Schiff base complexes compatible with assigned structure.
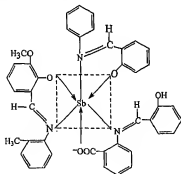
Fig : Proposed structure of mixed ligand complexes
[η²-ovmab)Sb (η²-osab) (η²-osaa)]

Table - 21

¹H NMR data (δ, ppm) of Antimony(III) complexes containing Schiff bases

Sl. No.	Compound	HC=N	Benzene	-OH	-OCH₃	Isopropoxide Bridging	Isopropoxide Terminal
1.	vnsbH	8.50	6.8-7.8	13.20	3.81	-	-
2.	[(Cl)₂ Sb(η²-ovnsnb)]	9.66	7.8-8.0	-	3.89	-	-
3.	[(Cl)₂ Sb(η¹-osnsb)]	9.76	6.9-8.0	-	-	-	-
4.	[(Cl) Sb(η²-ovnsnb)₂]	9.79	7.0-8.0	-	3.94	-	-
5.	[(Cl) Sb(η¹-osnsb)₂]	9.57	6.9-7.9	-	-	-	-
6.	[(OAc)Sb(η²-ovnsnb)₂]	9.63	6.8-7.7	-	3.89	-	-
7.	[(OAc)₂ Sb(η¹-osnsb)₂]	9.58	6.9-7.9	-	-	-	-
8.	[(η²-ovnsnb)₂ Sb(μ-OPrⁱ)₂{Al(OPrⁱ)₂}]	9.79	7.1-7.9	-	3.98	3.70-3.90	4.06-4.25
9.	[(η¹-osnsb)₂Sb(μ-OPrⁱ)₂{Al(OPrⁱ)₂}]	9.80	7.2-8.0	-	-	3.79-3.88	4.10-4.28

Table – 22

¹H NMR data (δ, ppm) of Antimony(III) complexes containing Schiff bases

Sl. No.	Compound	CH=N	Benzene	-OH	-OCH₃	Isopropoxide Bridging	Isopropoxide Terminal
1.	smabiH	8.30-8.60	6.8-7.8	13.40	-	-	-
2.	[(Cl)₂Sb(η¹-ssmab)]	9.59	6.9-8.0	-	-	-	-
3.	[(Cl)₂Sb(η¹-ovab)]	9.52	6.9-7.9	-	3.86	-	-
4.	[(Cl)Sb(η²-ssmab)₂]	9.64	6.8-8.0	-	-	-	-
5.	[(Cl)Sb(η²-ovab)₂]	9.72	7.0-8.0	-	3.94	-	-
6.	[(OAr)Sb(η²-smab)₂]	9.78	6.9-7.7	-	-	-	-
7.	[(OAr)Sb(η²-ovab)₂]	9.62	6.9-7.9	-	3.98	-	-
8.	[(η¹-ssmab)₂Sb(μ-OPⁱ₃)₂Al(OPⁱ₃)₂]	9.68	7.1-8.0	-	-	4.04-4.26	3.76-3.99
9.	[(η¹-ovab)₂Sb(μ-OPⁱ₃)₂Al(OPⁱ₃)₂]	9.63	7.2-7.9	-	3.96	4.10-4.28	3.70-3.88
10.	[(η¹-ossmab)Sb(η¹-ssab)(η¹-ovab)]	9.71	6.8-7.8	-	-	-	-

3.3.4 ^{13}C NMR Spectral Studies

The ^{13}C NMR spectra of the synthesised compounds recorded in DMSO-d_6 showed characteristic resonance due to the alkoxy, hydroxy, methoxy, phenyl and azometine groups. The spectral studies of metal complexes should be interpreted by comparison of spectra of ligands with that of corresponding complexes which leads following conclusion Table [23,24].

(i)   The ^{13}C NMR studies of ligands shows reasonable shift in the phenolic carbon from δ149.84 to 159.64 ppm.. The downfield shift in phenolic carbon atom showed coordination may occur from oxygen and Sb-O bond formation occurs.

(ii)   The Schiff bases showed singlet [138] at δ151.24 ppm due to azomethine carbon atom, which may be shifted downfield to δ160.15 ppm showing coordination of azomethine nitrogen to metal atom.

(iii) The ^{13}C signal appeared [139] in the region δ125.62, 138.50 and 122.70 ppm may be assigned to the three different carbon atoms of the benzene ring of ligand. There is no appreciable shift found in the carbon atom of benzene ring.

(iv)   In the ^{13}C NMR spectral data [140] of ligands (isatin derived) and their complexes, (IX, X, XI, XII, XIII, XIV, XV, XVI) the appreciable downfield shift in the position of amido carbon from δ166 to 170 ppm clearly indicate that covalent (Sb-O) bond formation may occur due to enolic form of ligand.

(v)   A sharp signal obtained for the methine [138] carbon of the
      terminal and bridging isopropoxy groups are observed in
      complexes (IIIb, VIb, VIIb, VIIIb) at δ60.18 to 60.52 ppm and
      δ61.16 to 64.42 ppm respectively, suggesting that Antimony
      and Aluminium atoms are bonded to each other with
      isopropoxy bridged carbon atom.

(vi) A sharp singlet showed [141] downfield shift of -COOH
      carbon atom [50] from δ170 to 162 ppm in comparison to free
      ligand showing that coordination (XIII, XIV), may occur
      through carboxyl oxygen in monodentate way.

(vii) Vanillidene Schiff base complexes of [142] Antimony (III)
      showed (I, III, IIIa, IIIb, IV, VII, VIIIa, VIIIb, IX, XII, XIV) a
      singlet at δ54.1 ppm, which is characteristic of m-OCH₃
      group.

      On the basis of above findings following structure may be
proposed.
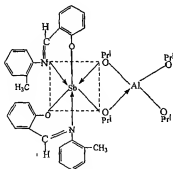
Fig. 29 Proposed structure of [(η²-osmab)₂Sb(μ-OPrⁱ)₂ {Al(OPrⁱ)₂}]

Table – 23

^{13}C NMR Spectral data (δ, ppm) of Antimony(III) complexes containing Schiff bases

Sl. No.	Complexess	-OH	Azomethine CH=N	Aromatic carbon	-COOH	OCH₃	Isopropoxide	
							Bridging	Terminal
1.	vmabH	145.89	151.60	132.50,125.67,122.70	-	54.1	-	-
2.	[(Cl)₂ Sb(η²-ovmab)]	162.20	159.12	145.60,126.79,121.30	-	53.17	-	-
3.	[(Cl)₂ Sb(η²-onab)]	161.18	152.16	143.20,121.80,121.97	-	-	-	-
4.	[(Cl) Sb(η²-ovmab)₂]	159.16	155.51	147.70,122.47,121.89	-	54.07	-	-
5.	[(Cl) Sb(η²-onab)₂]	157.19	157.31	139.40,125.69,120.60	-	-	-	-
6.	[(OAc) Sb(η²-ovmab)₂]	153.18	156.40	150.10,125.39,121.70	-	53.01	-	-
7.	[(OAc) Sb(η²-onab)₂]	157.70	158.60	143.80,126.19,121.90	-	-	-	-
8.	[(η²-ovmab)₂Sb(μ-OPⁱh₂)(Al(OPrⁿh₂)]	156.12	154.30	147.60,124.80,123.7	-	54.02	64.79	61.70
9.	[(η²-onab)₂Sb(μ-OPⁱ)₂(Al(OPrⁿ)₂)]	154.04	155.30	137.40,123.60,121.60	-	-	63.89	60.69
10.	[(η²-ovsa) Sb(η²-onab)(η²-olab)]	151.02	153.78	138.20,125.40,122.60	177.68	53.89	-	-

Table - 24

¹³C NMR Spectral data (δ, ppm) of Antimony(III) complexes containing Schiff bases

Sl. No.	Complexes	-OH	Azomethine CH=N	Aromatic carbon	-COOH	OCH₃	Isopropoxide Bridging	Terminal
1.	[(CH₃)₂Sb(η²-osmab)]	151.02	159.92	138.50,125.67,122.70	-	-	-	-
2.	[(C₂H₅)₂Sb(η²-ovsb)]	154.04	158.08	146.60,126.79,121.30	-	54.02	-	-
3.	[(C₆H₅)₂Sb(η²-ssmab)₂]	156.12	156.51	144.20,122.20,120.79	-	-	-	-
4.	[(C₆H₅)Sb(η²-ovsb)₂]	160.23	152.82	148.70,123.47,121.70	-	53.58	-	-
5.	[(OAc)₂Sb(η²-ssmab)₂]	153.23	150.11	138.40,124.69,119.60	-	-	-	-
6.	[(OAc)Sb(η²-ovsb)₂]	152.18	157.31	150.10,125.39,121.70	-	53.79	-	-
7.	[(η²-ssmab)₂Sb(μ-OPrⁱ)₂Al(OPrⁱ)₂]	156.14	152.28	143.80,126.19,121.90	-	-	64.42-	60.18
8.	[(η²-ovsb)₂Sb (μ-OPrⁱ)₂Al(OPrⁱ)₂]	158.16	155.51	147.60,124.80,123.70	-	54.03	64.59	61.10
9.	[(η²-ovmab)Sb(η²-osab)(η²-siab)]	160.18	150.16	137.40,123.60,121.60	-	54.03	-	-
10.	[(η²-ssau)₂Sb(η²-osab)(η²-oiab)]	161.20	159.12	138.20,125.40,122.60	178.30	-:-	-	-

3.4.4.5 Fab-mass Spectral Studies

The FAB-mass spectral investigation [199] was perform formed the representative complexes of Antimony (III) synthesized during the present course of investigation.

The FAB-mass spectrum of representative complex of dichloro such as $[(Cl)_2Sb(\eta^2\text{-osmab})]$ showed characteristic molecular ion $[M^+]$ peak at m/z = 403 correspond to the molecular weight of complex suggesting monomeric nature of the complexes.

$$[C_{14}H_{12}NOSbCl_2] \xrightarrow[-2e^-]{+e^-} [C_{14}H_{12}NOSbCl_2]^+$$

$$m/z = 403$$

$$\Big\downarrow -C_7H_7^{\cdot}$$

$$[C_7H_5NOSbCl_2]^+$$
$$m/z = 312$$

$$\Big\downarrow -OC_6H_4^{\cdot}$$

$$[SbCl]^+ \xleftarrow{-Cl^{\cdot}} [SbCl_2]^+ \xleftarrow{-HCN^{\cdot}} [CHNSbCl_2]^+$$
$$m/z = 157 \qquad m/z = 193 \qquad m/z = 220$$
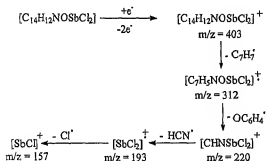
Scheme-3.1 FAB-mass fragmentation pattern of dichloro complexes of the type $[(Cl)_2Sb_2(\eta^2\text{-osmab})]$

The FAB-mass spectrum of monochloro complexes [(η^2-ovab)$_2$Sb(Cl)] exhibited molecular ion [M$^+$] peaks at m/z = 609 suggested monomeric nature of the complexes the fragmentation of the complex represented by following scheme.

$[C_{28}H_{24}N_2O_4SbCl] \xrightarrow[-2e^-]{+e^-} [C_{28}H_{24}N_2O_4SbCl]^{\cdot} \xrightarrow{-C_6H_5^{\cdot}} [C_{22}H_{19}N_2O_4SbCl]^{\ddagger}$

m/z = 609, m/z = 532(monomer)

$\downarrow - C_6H_5^{\cdot}$

$[C_{16}H_{14}N_2O_4SbCl]^+$
m/z = 455

$\downarrow - OCH_3^{\cdot}$

$[C_{15}H_{11}N_2O_3SbCl]^+$
m/z = 424

$\downarrow - OC_6H_5^{\cdot}$

$[C_9H_6N_2O_2SbCl]^+$
m/z = 333

$[SbCl]^+$
m/z = 157

$[C_8H_7NO_2SbCl]^{\ddagger}$
m/z = 306

$\downarrow - OCH_3^{\cdot}$

$[CH_3OSbCl]^+ \xleftarrow{- HCN} [C_2H_4NOSbCl]^+ \xleftarrow{- OC_6H_3^{\cdot}} [C_8H_7NO_2SbCl]^{\ddagger}$
m/z = 188 $\qquad$ m/z = 215

$\downarrow - HCN$
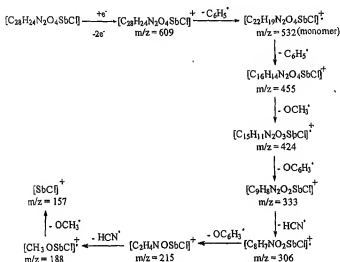
Scheme-3.2 FAB-mass fragmentation pattern

[(Cl)Sb(η^2-ovab)$_2$)]
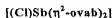
The FAB-mass spectrum of mixed ligand complexes of the type $[(\eta^2\text{-ovmab})Sb(\eta^2\text{-osab})$ $(\eta^2\text{-oiab})]$ exhibited molecular ion peak $[M^+]$ at m/z 779 suggesting monomeric nature of the complexes. The fragmentation of the complex represented by following scheme 3.3.

$[C_{42}H_{33}N_4O_4Sb]$ $\xrightarrow[-2e^-]{+e^-}$ $[C_{42}H_{33}N_4O_4Sb]^+$ $\xrightarrow{-C_6H_5^\bullet}$ $[C_{36}H_{28}N_4O_4Sb]^+$
m/z = 779   m/z = 702(monomer)

$\downarrow -C_4H_9^\bullet$

$[Sb]^+$ $[C_{30}H_{23}N_4O_4Sb]^+$
m/z = 121   m/z = 625

$\uparrow -C_6H_3N^\bullet$ $\downarrow -OCH_3^\bullet$

$[C_6H_3N\ Sb]^{+}$ $[C_{29}H_{20}N_4O_3Sb]^+$
m/z = 211   m/z = 594

$\uparrow -N=C=O^\bullet$ $\downarrow -OC_6H_3^\bullet$

$[C_7H_3N_2OSb]^+$ $[C_{23}H_{17}N_4O_2Sb]^+$
m/z = 253   m/z = 503

$\uparrow -HCN^\bullet$ $\downarrow -C_6H_7^\bullet$

$[C_8H_5N_3OSb]^+$ $\xleftarrow{-C_7H_3O^\bullet}$ $[C_{15}H_9N_3O_2Sb]^+$ $\xleftarrow{-HCN^\bullet}$ $[C_{16}H_{10}N_4O_2Sb]^{+}$
m/z = 280   m/z = 385   m/z = 412
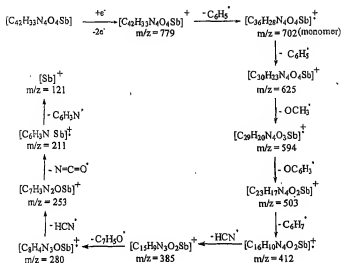
Scheme-3.3 FAB-mass Fragmentation Pattern of mixed ligand complexes

$[(\eta^2\text{-ovmab})Sb(\eta^2\text{-osab})(\eta^2\text{-oiab})]$
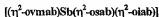
Chapter-IV

EXPERIMENTAL

4.1 GENERAL INTRODUCTION

4.1.1 Apparatus:

The glass apparatus with interchangeable standard joints were used throughout the experimental work. The apparatus was carefully cleaned and rinsed with rectified spirit before placing it in an oven maintained temperature at 120-150°C. The apparatus was then cooled either in desiccator or fitted with guard tubes filled with anhydrous silica gel special weighing tube with standard joint were used for the sampling of compound for analytical purposes.

4.1.2 Materials

All the chemicals used throughout the course of experimental work were of G.R. or Analar grade and spectroscopic grade solvents were employed for recording the spectra.

Sodium metal (B.D.H.,) was used after cleaning the exposed surface and soaking the adhered liquid with filter papers. *Aluminium metal* (B.D.H.) was used after scratching out the outer surface with sand paper. Benzene (B.D.H.) o-vanilline (Lancaster) normal propanol (B.D.H.), isopropanol (B.D.H.) and methanol (Loba), pyridine (B.D.H.,) quinoline (BDH) Antimony trichloride (Loba), Aluminium trichloride (CDH) grade have been used. Aluminium isopropoxide was prepared [197] by dissolving Aluminium foil in isopropanol in the presence of $HgCl_2$ as catalyst and refluxing it for ~6h. Final product was purified by distillation (bp 95°C) under reduced pressure.

4.1.3. Analytical methods

Before adopting any of the quantitative methods of analysis for the newly synthesized compounds, the method was standardised by repeated analyses of a prepared mixtures containing the same metals and the conditions were predetermined under which the estimation could be relied with maximum possible accuracy.

4.1.3.1 Elemental Analyses

1-   Estimation of Aluminium

A weighed amount of appropriate sample was taken in a conical flask in the presence of HCl and evaporated to dryness then added 100 ml. water and heated upto 70-80°C & filtered. Now 2% of 8-hydroxyoxinate solution in conical flask upto complete precipitation followed by 0.4g ammonium acetate (for complete precipitation) and heated till boiling. The reaction mixture was cooled and filtered in centered glass crucible and washed with warm water. The colour of precipitated changed from greenish yellow to pale yellow.

$$\% \text{ of Al} = \frac{5.88 \times \text{Wt. of Precipitate}}{\text{Weight of sample}}$$

2.   Estimation of Antimony

A weighed amount of sample of the compound was decomposed with a mixture of conc. H_2SO_4 and HNO_3 and heated to remove nitric acid. The resulting antimony solution was reduced with sulphurous acid and the Sb(III) precipitated as sulphide. The

precipitate after filtration was dissolved in concentrated. HCl using indicator naphthalene black, titrated slowly with standard 0.02 potassium bromates with constant stirring of the solution as the 2-3 seconds between the drops until the colour of solution is changed from colourless to vary pale yellow. If colour of indicator faded, add another drop of indicator solutions, the immediate discharge of colour indicates equivalent points has been passed and titration is completed.

3. Estimation of Chloride

Chloride contents were estimated by Volhard's method [198] silver nitrate [25cm³(0.1N)] solution was taken into conical flask followed by the addition of 6N HNO₃ (5cm³) in which weighed amount of sample (to be analysed) was dissolved. It was shaken well in the presence of ~5 cm³ nitrobenzene for ~15 minutes and then titrated against 0.1N ammonium thiocyanate solution in the presence of ferric alum indicator till the colour changed from light brown to red brown (i. e. end point)

$$\% \, of \, Cl = \frac{0.3548 \times (Blank \, reading - Reading \, with \, compound)}{Weight \, of \, compound}$$

4.1.3.2 Estimation of isopropoxy in the complex compound

Isopropoxide content in the corresponding isopropoxy derivatives were estimated by an oxidimetric method [199-200]. The method consist of pipetting 5 cm³ of standard chromic acid (Normal

potassium dichromate in 12.5% conc. sulphuric acid) into a semi micro well stoppered bottle and transferring a weighed amount of appropriate sample to this solution. The reactant in the stoppered bottle and transferring a weighed amount of appropriate sample into this solution.

The reactant in the stoppered bottle were allowed to stand for two hours preferably at about 0-5°C the content of the bottle were transferred into a 500 cm^3 conical flask, containing a solution of 4g of sodium bicarbonate and 6g of potassium iodide in water in which 10cm^3 of concentrated hydrochloride acid was already added to provide an atmosphere of carbon dioxide during the process of titration in order to prevent air oxidation of the reactant. The liberated iodine was then titrated with standard 0.2 N sodium thiosulphate solution using starch as indicator. Blank determination was set up at the same time maintaining all the conditions identical except excluding sample for analysis.

The volume of potassium dichromate required for oxidation of isopropoxy was measured by difference between the blank and test determinations the isopropoxy content were determined by the following formula.

$$\% \text{ of isopropoxy} = \frac{(\text{Blank} - \text{Volume of hypo consumed}) \times \text{Equ weight of isopropoxy}}{2 \times \text{Blank} \times \text{Weight of compound}}$$

Infrared spectra

Infra red spectra were recorded as nujol mull using Perkin Elmer 1000 FTIR spectrometer(4000-200 cm^{-1})

Electronic spectra

Electronic spectra of the compound were recorded either DMSO and/or tetrahydrofuron using (200-850 nm) using Elmer Lambda 15 Spectrophotometer.

Nuclear magnetic resonances (^{1}H and ^{13}C NMR) spectra

The NMR spectra of complexes were recorded in DMSO-d$_6$/CDCl$_3$ in Bruker DRX-300 MHz-FTNMR spectrometer with low and high temperature facility -90 to +80 ^{0}C.

FAB-mass spectra

The FAB-mass spectra were recorded on JEOLSX-102. FAB-mass spectrometer (Data system Using Argon/Xenon (6 kv, 10 mA) as the FAB gas was the accelerating voltage was 10 kV and spectra were recorded at room temperature, m-nitrobenzyl alcohol (NBA) was used as the matrix.

## 4.2 PREPARATION OF LIGANDS

4.2.1 Preparation of Schiff bases

(i) Salicylidene-2-methyl-1-aminobenzene (smabH) [201]

Salicylaldehyde (4.88cm^3, 46.59 mmol) and toluidine (2-methyl-1-aminobenzene) (5.01 cm^3, 46.59 mmol) in methanol

(~25cm³) was refluxed for ~6h to afford yellow coloured solution. The solution was kept overnight to afford yellow crystals of composition $C_{14}H_{13}NO$. The product obtained was recrystallised in ethanol and dried under reduced pressure to afford analytically pure bright yellow coloured compound (smabH) 76% yield. Analysis, found (Calcd), C 79.64 (79.58), H 6.25 (6.20), N 6.67 (6.61) (mp 60°C).
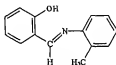
Salicylidene-2-methyl-1-aminobenzene (smabH)

(ii) Salicylidene-3-nitro-1-aminobenzene [snabH] [202]

To the solution of 3-nitroaniline (3-nitro-1-aminobenzene) (4.00g, 28.96 mmol) in methanol (~30 cm³) salicylaldehyde (3.03cm³, 28.96 mmol) was added gradually with constant stirring and refluxed for ~3h on cooling a dark yellow solid of composition $C_{13}H_{10}N_2O_3$ was obtained, which was purified by recrystallisation in ethanol and dried under reduced pressure to afford yellow coloured compound in ~75% yield (m.p. 121°C). Analysis found, (Calcd), C 63.88 (64.45), H 4.01 (4.16), N 1138 (11.56).
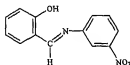
salicylidene-3-nitro-1-aminobenzene (snabH)

(iii) Salicylidene-1-aminobenzene [sabH] [203,204]

Equimolar amount of salicylaldehyde (4.50 cm^3, 42.95 mmol) and aniline (aminobenzene) (4.00 cm^3, 42.95 mmol) in methanol (~30 cm^3) was refluxed for ~4h to yield yellow crystals of composition $C_{13}H_{11}NO$. It was further recrystallised in ethanol and dried under reduced pressure to afford yellow coloured pure compound ~72% yield (mp 52°C). Analysis found (Calcd), C 79.21 (79.15), H 5.53 (5.62), N 7.12 (7.10).
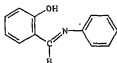
Salicylidene-1-aminobenzene (SabH)

(iv) Vanillidene-2-methyl-1-aminobenzene (vmabH) [205]

Equimolar amount of vanillin (2-hydroxy-3-methoxy benzaldehyde) (4.76g, 31.31 mmol) and o-toluidine (2-methyl-1-aminobenzene) (3.35g, 31.31mmol) in methanol (~25 cm^3) was refluxed for ~6h to afford a light yellow coloured solution. The solution was kept overnight to afford light brown coloured crystals of composition $C_{15}H_{15}O_2N$. The product was recrystallised in ethanol and dried under reduce pressure to afford analytically pure light brown coloured compound (vmabH) 78% yield (m.p. 101°C) Analysis, found (Calcd), C 74.24(74.68), H 6.42 (6.22), N 5.61 (5.80).
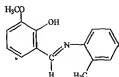
Vanillidene-2-methyl-1- aminobenzene (vmabH)

(v)   **Vanillidene -1-aminobenzene (vabH)[205]**

To the solution of vanillin (2-hydroxy-3-methoxy benzaldehyde) (6.42g, 42.21mmol) in methanol (50cm³), aniline (aminobenzene) (4.17 cm³ 42.21 mmol) was added with constant stirring and refluxed for (~4h) on cooling dark yellow coloured crystals of composition $C_{14}H_{13}O_2N$ was obtained, which was purified by recrystallisation in ethanol and dried under reduced pressure to afford dark yellow coloured compound, off 75% yield (m.p. 99ºC).   Analysis found (Calcd), C 74.32 (74.00), H 6.02 (5.72), N 5.89 (6.16)
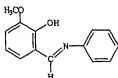
Vanillidene -1-aminobenzene (vabH)

(vi)   **Isatidene-3-nitro-1-aminobenzene (InabH) [206]**

A methanolic solution (30 cm³) of isatin (5.22 g 35.5 mmol) was added to methanolic solution of 3-nitroaminobenzene (4.90g, 35.5 mmol) with constant stirring and refluxed for ~4h. On cooling a red solid of composition $(C_{14}H_{10}N_3O_3)$ was obtained, which was

purified by THF-benzene mixture and dried under reduced pressure to afford red coloured compound in 75% yield. Analysis, found (Calcd), C 62.8 (62.86), H3.46(3.36), N15.81(15.71).
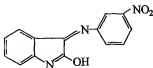
Isatidene-3-Nitro-1-Aminobenzene (inabH)

(vii) Isatidene-1-aminobenzene (IabH) [207]

To the solution of isatin (6.34 g, 43.12 mmol) in methanol ($\sim$50 cm^3), aniline (aminobenzene) 4.10 cm^3 43.12 mmol) was added gradually with constant stirring and refluxed for $\sim$3h. On cooling pink solid of composition $C_{14}H_{10}N_2O$ obtained which was purified by recrystallization in the THF-Benzene mixture, and dried under reduced pressure to afford pink coloured compound, 78% yield. Analysis, found (Calcd) C75.83(75.58), H12.61(12.59), N4.91(4.49)
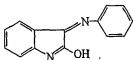
Isatidene aminobenzene (IabH)

(viii) 4-Nitrobenzylidene-2-aminophenol (nbaphH) [208]

A methanolic solution ($\sim$30 cm^3) of 4-nitrobenzaldehyde (5.53g, 36.65 mmol) was added to methanolic solution of 2-aminophenol (4.00 g, 36.65 mmol) with constant stirring and refluxed for ($\sim$4h) to give brown coloured solution, which on cooling

at room temperature afforded compound of composition $C_{13}H_{10}N_2O_3$. This isolated compound was further purified by recrystallisation in THF-benzene mixture and dried under reduced pressure to yield brown coloured compound was found to be (76% (mp 150°C). Analysis, found (Calcd) C63.76(64.45), H4.08(4.16s), N11.22(11.56).
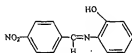
4-nitrobenzylidene-2-aminophenol (nbaphH)

(ix) Salicylidene-anthranilicacid (saaH) [209]

Salicylaldehyde (3.03 cm³, 28.96 mmol) was added gradually to a methanolic solution (30 cm³) of anthranilicacid (4.00g, 28.9 mmol) with constant stirring and allowed to reflux for ~4h. The reaction mixture on cooling at room temperature, afforded brown coloured product, which was recrystallised in ethanol and dried under reduced pressure to afford analytically pure light brown coloured compound in 80% yield (mp 180°C) having molecular formula $C_{14}H_{11}NO_3$. Analysis found (Calcd), C69.72(69.69), H4.58(4.59), N5.75(5.80).
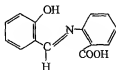
Salicylidene -anthranilicacid (saaH)

(x) Vanillidene-anthranilicacid (vaaH) [210]

To a solution of vanillin (4-hydroxy-3-methoxy benzaldehyde) (5.477g, 36.0 mmol) in methanol (~30cm^3), methanolic solution of anthranilicacid (4.973g, 36.0 mmol) was added gradually with constant stirring and refluxed for ~5h to obtain yellow coloured solid product. This product was purified by recrystallisation to afford analytically pure yellow coloured ligand in 78% yield (mp 155). Analysis found (Calcd) C66.23(66.41), H4.75(4.83), N5.10(5.16).
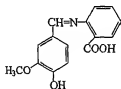
Vanillidene-anthranilicacid (vaaH)

4.2.1 Preparation of sodium phenolate Na(OAr)

Equimolar amount of 4-nitrophenol (0.222 g, 1.60 mmol) and sodium metal (0.038g, 1.60) was taken in isopropanol (~30 cm^3) refluxed for ~2h to afford orange coloured sodium salt of 4-nitrophenol.

4.2.3 Preparation of sodium tetraalkoxyaluminate

Sodium tetraalkoxyaluminate was prepared by literature procedure [211].

4.3 SYNTHESIS OF COMPLEXES

During present course of investigations, various complexes of Aluminium (III) and Antimony (III) have been synthesised. Since in most of the cases preparative procedures are similar there for details are given below only for typical cases for the sake of brevity. Analytical details have been summarised in Table.[25-32]

4.3.1 Synthesis of Aluminium (III) Complexes

4.3.1.1 Preparation of dichloro complexes of the types [(μ-Cl)$_2$Al$_2$(Cl)$_2$(η^2-ovmab)$_2$] and [(μ-Cl)$_2$Al$_2$(Cl)$_2$ (η^2-osnabH)$_2$]

To a solution of Na(ovmab) (.352 g, 1.34) in benzene (˜30cm^3) prepared by refluxing sodium metal (0.030 g, 1.34) in isopropanol (~5 cm^3) and vmabH (0.323,g, 1.34 mmol) in benzene was added AlCl$_3$ (anhydrous) (0.178g, 1.34 mmol) in benzene was added to a solution of methanol-benzene mixture was refluxed/stirred for ~4h during which time colour of reaction mixture was changed from light yellow to dark yellow.

The precipitated NaCl(0.078g, 1.34mmol) was removed by filtration and filtrate was concentrated by distillation and dried under reduced pressure to produce light brown solid, which was purified by recrystallisation in benzene-methanol afford light brown coloured solid product [(μ-Cl)$_2$Al$_2$(Cl)$_2$(η^2-ovmab)$_2$] (0.288g, 64%)

By similar method Aluminium (III) complexes of the type [(μ-Cl)$_2$Al$_2$(Cl)$_2$(η^2-osnab)$_2$] has been prepared details are collected in Table - [25]

4.3.1.2 Preparation of monochloro complexes of the types [(μ-Cl)$_2$Al$_2$(η^2-ovmab)$_4$] and [(μ-Cl)$_2$ Al$_2$ (η^2-osnab)$_4$]

To a stirred hot solution of anhydrous AlCl$_3$ (0.118g, 0.89mmol) in dry benzene (~20cm^3) was added a freshly prepared Na(ovmab) (0.468g, 1.78mmol) [prepared by adding vmabH (0.429g, 1.78, mmol) dissolved in benzene (25-cm^3) to a solution of isopropanol (~5cm^3) containing sodium metal (0.040g, 3.25mmol)] and conteht was refluxed/stirred for ~5h during which time colour of the reaction mixture changed from light yellow to black.

After filtering off precipitated NaCl (0.104g,.1.78 mmol) the filtrate was concentrated to about (~10cm^3) by distillation and stripped of under reduced pressure to afford a black colour powdered solid. The product was further purified by recrystallisation using methanol-benzene mixture to obtain a black coloured powdered solid [(μ-Cl)$_2$Al$_2$(η^2-ovmab)$_4$][0.355g, 74%.]

A similar process have been adopted for synthesis of Aluminium (III) complexes of the type [(μ-Cl)$_2$Al$_2$(η^2-osnab)$_4$], [(μ-Cl)$_2$Al$_2$(η^2-ovab)$_4$] & [(μ-Cl)$_2$Al$_2$(η^2-osmab)$_4$], synthesised details are summarised in table [26]

Table 25

Synthetic and analytical details of dichloro Aluminium (III) complexes containing Schiff bases

Sl. No.	Reactants (g, mmol)		Products (g, % yield)		% Analysis Found (Calcd.)	
					Al	Cl
1.	AlCl₃ (0.176g, 1.34mmol)	+ Na(ovnmab)] (0.352g, 1.34mmol)	[(μ-Cl)₂ Al₂(Cl)₂(l¹'-ovnmab)] (0.288g, 64)	(I)	7.12 (7.98)	17.13 (18.28)
2.	AlCl₃ (0.160g, 1.20mmol)	+ Na(smab)] (0.316g, 1.20mmol)	[(μ-Cl)₂ Al₂(Cl)₂(l¹'-smab)] (0.268g, 66)	(II)	7.94 (8.08)	19.05 (20.93)
3.	AlCl₃ (0.176g, 1.30mmol)	+ Na(osmab)] (0.307g, 1.32mmol)	[(μ-Cl)₂ Al₂(Cl)₂(l¹'-osmab)] (0.281g, 68)	(V)	7.67 (8.73)	21.30 (22.96)
4.	AlCl₃ (0.160g, 1.25mmol)	+ Na(ovab)] (0.311g, 1.25mmol)	[(μ-Cl)₂ Al₂(Cl)₂(l¹'-ovab)] (0.298g, 74)	(VI)	11.33 (12.04)	20.74 (21.74)

Table-26

Synthetic and analytical details of monochloro Aluminium (III) complexes containing Schiff bases

Sl. No.	Reactants (g, mmol)		Products (g, % yield)	% Analysis Found (Calcd.)	
				Al	Cl
1.	AlCl₃ (0.118g, 0.89mmol)	+ 2Na(ovmab) (0.468g, 1.78mmol)	[(μ-Cl)₂ Al(η²-ovmab)]₂ (III) (0.355, 74)	4.13 (4.97)	5.33 (6.52)
2.	AlCl₃ (0.160g, 1.20mmol)	+ 2Na(cmab) (0.633g, 2.40mmol)	[(μ-Cl)₂ Al(η²-cmab)] (IV) (0.444, 68)	4.95 (4.87)	5.29 (6.51)
3.	AlCl₃ (0.140g, 1.05mmol)	+ 2Na(osmab) (0.488g, 2.10mmol)	[(μ-Cl)₂ Al(η²-osmab)] (VII) (0.359, 71)	4.86 (5.59)	6.96 (7.35)
4.	AlCl₃ (0.126g, 0.95mmol)	+ 2Na(ovab) (0.472g, 1.90mmol)	[(μ-Cl)₂ Al(η²-ovab)] (VIII) (0.360, 74)	4.32 (5.24)	6.09 (6.89)

4.3.2 Synthesis of Antimony (III) complexes

4.3.2.1 Preparation of dichloro complexes of the type [(η²-ovmab)Sb(Cl)₂] and [(η²-osnab) Sb(Cl)₂]

To a stirred hot suspension of anhydrous SbCl₃ (0.296g, 1.30mmol) in benzene (~20 cm³) added freshly prepared Na(ovmab) (0.342g, 1.30mmol) [prepared by refluxing sodium metal (0.030g, 1.30mmol) in isopropanol (~5 cm³) and vmabH (0.342g, 1.30 mmol) in then the reaction mixture was refluxed for 4 hour during the course of reaction the colour of the solution was changed from light yellow to dark yellow.

After filtering off precipitated NaCl (0.076g, 1.30 mmol) the filtrate was concentrated by distillation and stripped off under reduced pressure to afford a light yellow coloured powdered solid. The product was further purified by recrystallisation using benzene-methanol mixture and dried under reduced pressure to obtain light yellow coloured solid [(η²-ovmab)Sb(Cl)₂] (0.448g, 86.8%)

The complex [(η²-osnab)Sb(Cl)₂] was synthesized analogously the pertinent data listed in Table. Similar procedure have been adopted for synthesis of antimony (III) containing Schiff bases such as smabH, vabH, experimental and analytical details summarised in table [27].

4.3.2.2 Preparation of monochloro complexes of the type [(η²-ovmab)₂Sb(Cl)] and [(η²-onsab)₂Sb(Cl)]

To a stirred hot suspension of anhydrous SbCl₃ (0.425g, 1.86mmol) in benzene (~20 cm³) was added freshly prepared Na(ovmab) (0.979g, 3.72mmol) [prepared by refluxing vmabH (0.897g, 3.72mmol) dissolved in benzene (20 cm³) and solution of methanol (~5cm³) containing sodium metal (0.085g, 3.72mmol)] then this reactant mixture refluxed/stirred for 5 hour during the course of reaction, the colour of the solution changed from light yellow to reddish yellow.

After filtering off precipitated NaCl(0.217g, 3.72mmol) obtained & the filtrate was concentrated by distillation and stripped off under reduced pressure to afford a dark yellow powdered solid. The product was further purified by recrystallisation using benzene - methanol mixture and dried under reduced pressure to obtain dark yellow coloured solid [(η²-ovmab)₂Sb (Cl)] (0.817g, 64%).

The complex [(Cl)Sb(η²-osnab)₂] was synthesized analogously the pertinent data for this listed in Table. Similar procedure has been adopted for synthesis of antimony (III) containing Schiff bases such as smabH and vabH, experimental and analytical details summarised in table [28].

Table-27

Synthetic and Analytical details of Dichloro Antimony (III) complexes containing Schiff bases

Sl. No.	Reactants (g, mmol)			Products (g, % yield)		% Analysis Found (Calcd.)	
						Sb	Cl
1.	SbCl₃ (0.296g, 1.30mmol)	+	Na(ovanb)] (0.342g, 1.30 mmol)	[(η²-ovanb)Sb(Cl)₂] (0.488, 86.8)	(I)	27.98 (28.08)	15.98 (16.38)
2.	SbCl₃ (0.278g, 1.22mmol)	+	Na(csnab)] (0.322g, 1.22mmol)	[(η²-csnab)Sb(Cl)₂] (0.432, 72)	(II)	27.00 (28.08)	15.00 (16.38)
3.	SbCl₃ (0.258g, 1.13mmol)	+	Na(csnnab)] (0.263g, 1.13mmol)	[(η²-csnnab)Sb(Cl)₂] (0.377, 82)	(V)	29.68 (30.14)	16.32 (17.54)
4.	SbCl₃ (0.264g, 1.16mmol)	+	Na(ovab)] (0.289g, 1.16mmol)	[(η²-ovab)Sb(Cl)₂] (0.391, 80)	(VI)	29.00 (29.06)	15.93 (16.95)

Table-28

Synthetic and analytical details of monochloro Antimony (III) complexes containing Schiff bases

Sl. No.	Reactants (g, mmol)			Products (g, % yield)	% Analysis Found (Calcd.)	
					Sb	Cl
1.	SbCl₃ (0.425g, 1.86mmol)	+	2Na(ovnab) (0.979g, 3.72mmol)	[tr²-ovnab)₂Sb(Cl)] (III) (0.817, 64)	18.97 (19.08)	5.02 (5.56)
2.	SbCl₃ (0.262g, 1.15mmol)	+	2Na(osnab) (0.607g, 2.30mmol)	[tr²-osnab)₂Sb(Cl)] (IV) (0.646, 88)	18.68 (19.03)	5.12 (5.50)
3.	SbCl₃ (0.281g, 0.123mmol)	+	2Na(osmab) (0.575g, 2.47mmol)	[tr²-osmab)₂Sb(Cl)] (VII) (0.626, 88)	20.97 (21.07)	5.79 (6.14)
4.	SbCl₃ (0.359g, 1.57mmol)	+	2Na(ovab) (0.782g, 3.14mmol)	[tr²-ovab)₂Sb(Cl)] (VIII) (0.748, 78)	19.02 (19.97)	5.09 (5.82)

4.4 REACTIONS OF MONOCHLORO COMPLEXES

During the present course of investigations, various types of monochloro complexes of Aluminium (III) and Antimony (III) have been synthesised and their reactions with various sodium salts such as Na((OAr) and [(Na{(AlOpr^i)}$_4$] have been carried out.

4.4.1 Reactions of [(μ-Cl)$_2$Al$_2$(η^2-ovmab)$_4$] and [(μ-Cl)$_2$Al$_2$(η^2-osnab)$_4$]

(i) With Sodium Phenolate

A freshly prepared solution of sodium phenolate Na(OAr) (1.93g, 1.20mmol) in (benzene ~20cm^3) [prepared by the reaction of sodium metal (0.027g, 1.20mml) dissolved in isopropanol (~5cm^3) and 4 nitrophenol (0.167g, 1.20 mmol) dissolved in benzene ~20 cm^3] was added to pre-stirred hot suspension of [(μ-Cl)$_2$Al$_2$(η^2-ovmab)$_4$] (0.651g,1.20 mmol) in benzene-methanol mixture, after refluxing for ~6h, colour of reaction mixture changed from light green to dirty yellow colour.

The precipitated NaCl (0.070g, 1.20 mmol) was removed by filtration and excess solvent was removed by distillation under reduced pressure to obtain light yellow coloured, solid product, which was purified by recrystallisation from benzene-methanol mixture to give [(η^2-ovmab)$_2$Al$_2$(μ-OAr)$_2$] (0.602g, 78%).

Similar method were adopted to prepare [(η^2-osnab)$_4$Al$_2$(μ-OAr)$_2$] the experimental details are collected in the table [29].

(ii) **With Sodium tetraalkoxyaluminate**

To a stirred hot solution of $[(\mu\text{-Cl})_2 \, Al_2(\eta^2\text{-ovmab})_4]$ (0.651g, 1.20 mmol) in benzene-methanol mixture was added (~30 cm^3) solution of sodium tetraisopropoxyaluminate $Na\{Al(O Pr^i)_4\}$ (0.343g,1.20mmol) [Prepared by dissolving sodium metal (0.027g, 1.20mmol) in isopropanol (~5cm^3) and tetraisopropoxyaluminate (0.316g, 1.20mmol) in benzene] the reaction mixture was stirred for 2-h] followed by refluxing for ~5h, during which time the colour of the solution changed from light yellow to yellow.

The precipitated NaCl (0.070g, 1.20 mmol) was removed by filtration and excess solvent was removed from filtrate by distillation. The product was purified by recrystallisation from benzene-n-hexane mixture to give yellow coloured solid powdered solid $[(\eta^2\text{-ovmab})Al\{Al(\mu\text{-OPr}^i)_4\}]$ (0.609g, 66%).

Similar method was used for synthesis of $[(\eta^2\text{-osnab})Al\{Al(\mu\text{-OPr}^i)_4\}]$. The experimental and analytical details have been summarised in the Tables[29].

4.4.2 Reactions of $[(\eta^2\text{-ovmab})_2Sb(Cl)]$ and $[(\eta^2\text{-osnab})_2Sb(Cl)]$

(i) **With Sodium Phenolate [Na(OAr)]**

A freshly prepared solution of sodium phenolato[Na(OAr)] (0.080g, 0.55 mmol) in benzene (~20cm^3) [prepared by dissolving sodium metal (0.012g, 0.55mmol) in isoproponal (~5cm^3) and

4-nitrophenol (0.076g, 0.55mmol) in benzene ~30 cm³ was added to pre-stirred hot suspension of [(η²-ovmab)₂Sb(Cl)] (0.350g, 0.55mmol) in benzene-methanol mixture. After refluxing the reaction mixture for ~ 6h, colour of reaction mixture changed from dark yellow to light yellow.

The precipitated NaCl was removed by filtration and excess solvent was removed by distillation under reduced pressure to obtain whitish yellow coloured solid product, which was purified by recrystallisation from benzene-methanol mixture to give whitish yellow coloured powdered solid to give [(η²-ovmab)Sb(OAr)] (0.308, 78%).

Similar method was adopted to prepare [(η²-osnab)Sb(OAr)] the experimental details are collected in the table [31].

(ii) With sodium tetraalkoxyaluminate Na{Al(Oprⁱ)₄}

To a stirred hot yellow suspension of [(η²-ovmab)₂Sb(Cl) (0.401g, 0.55mmol) in benzene-methanol mixture was added solution to sodium tetraisopropoxyaluminate Na{Al(Oprⁱ)₄} (0.180g, 0.55mmol) [prepared by dissolving sodium metal (0.012g, 0.55mmol) in isopropanol (~5cm³) and tetraisopropoxyaluminate (0.145g, 0.55mmol) in benzene (~30cm³).] The reaction mixture was stirred for 2-h followed by refluxing for ~5h, during which time colour of suspension changed from dark yellow to light yellow.

The precipitated NaCl (0.0321g, 0.55mmol) was removed by filtration and excess solvent was removed from filtrate under reduce pressure to afford pink coloured solid. The product was recrystallisation in benzene-n-hexane mixture to give a powdered solid [(η^2-ovmab)Sb(μ-OPr^i)$_2$Al(OPr^i)] (0.349g, 67%).

Similar method was used for the synthesis of [(η^2-osnab) Sb(μ-OPr^i)$_2$]Al(OPr^i)] the pertinent data for the listed in Table[30].

The reaction of mono chloro complexes of Antimony (III) containing Schiff bases such as vabH and smabH have been carried out by using various sodium salt of phenol, alkoxide in equimolar ratio the experimental and analytical details have been summarised in the Tables [30].

Table-29

Synthetic & analytical details for the reactions of monochloro Aluminium (III) complexes containing Schiff bases

Sl. No.	Reactants (g, mmol)		Products (g, % yield)		% Analysis Found (Calcd.)	
					Al	OPr^i
1.	[(μ-Cl)₂ Al₂(η²-vmab)₂] (0.651g, 1.20mmol)	+ NaOAr (0.193g, 1.20mmol)	[(η¹-ovmab)₂Al₂(μ-OAr)₂] (0.602, 78)	IIIa	2.04 (2.09)	—
2.	[(μ-Cl)₂ Al₂(η²-smab)₂] (0.571g, 1.05mmol)	+ NaOAr (0.169g, 1.05mmol)	[(η¹-osmab)₂Al₂(μ-OAr)₂] (0.454, 68)	IVa	4.07 (4.17)	—
3.	[(μ-Cl)₂ Al₂(η²-smab)₂] (0.473g, 0.98mmol)	+ NaOAr (0.157g, 0.98mmol)	[(η¹-osmab)₂Al₂(μ-OAr)₂] (0.407, 71)	VIIa	3.20 (4.61)	—
4.	[(μ-Cl)₂ Al₂(η²-vmab)₂] (0.525g, 1.02mmol)	+ NaOAr (0.164g, 1.02mmol)	[(η²-ovmab)₂Al₂(μ-OAr)₂] (0.427, 68)	VIIIa	3.68 (4.37)	—
5.	[(μ-Cl)₂ Al₂(η²-vmab)₂] (0.651g, 1.20mmol)	+ Na₂[Al(OPr^i)₄] (0.343g, 1.20mmol)	[(η²-ovmab)₂ (μ-OPr^i)₂ Al₂{(OPr^i)₂}] (0.609, 66)	IIIb	3.30 (3.50)	14.48 (15.04)
6.	[(μ-Cl)₂ Al₂(η²-smab)₂] (0.599g, 1.09mmol)	+ Na₂[Al(OPr^i)₄] (0.311g, 1.09mmol)	[(η²-osmab)₂ (μ-OPr^i)₂ Al₂{(OPr^i)₂}] (0.562, 67)	IVb	3.08 (3.49)	13.97 (15.04)
7.	[(μ-Cl)₂ Al₂(η²-smab)₂] (0.420g, 0.87mmol)	+ Na₂[Al(OPr^i)₄] (0.248g, 0.87mmol)	[(η¹-smab)₂Al (μ-OPr^i)₂ {Al₂(OPr^i)₄}] (0.438, 71)	VIIb	2.93 (3.80)	15.02 (16.35)
8.	[(μ-Cl)₂ Al₂(η²-vmab)₂] (0.489g, 0.92mmol)	+ Na₂[Al(OPr^i)₄] (0.263g, 0.92mmol)	[(η¹-ovmab)₂Al-OPr^i]₂[Al(OPr^i)₄] (0.518, 76)	VIIIb	3.63 (3.63)	14.31 (15.64)

Table-30

Synthetic and analytical details and reactions of monochloro complexes of monoorgano (III) Containing Antimony Schiff bases

Sl. No.	Reactant (g, mmol)	Products (g, % yield)		% Analysis Found (Calcd.)		
				Sb	Al	OPr^i
1.	[Cl] Sb(η²-ovmab)₂] (0.343g, 0.50mmol) + NaOAr (0.080g, 0.50mmol)	[(η²-ovmab)₂Sb(OAr)] (0.308, 78)	IIIa	16.04 (16.44)	-	-
2.	[Cl] Sb(η²-osmab)₂] (0.383g, 0.60mmol) + NaOAr (0.096g, 0.60mmol)	[(η²-osmab)₂Sb(OAr)] (0.298, 68)	IVa	16.06 (16.40)	-	-
3.	[Cl] Sb(η²-osmab)₂] (0.323g, 0.50mmol) + NaOAr (0.090g, 0.50mmol)	[(η²-osmab)₂Sb(OAr)] (0.251, 76)	VIIa	16.79 (17.89)	-	-
4.	[Cl] Sb(η²-ovab)₂] (0.378g, 0.60mmol) + NaOAr (0.099g, 0.60mmol)	[(η²-ovab)₂Sb(OAr)] (0.359, 83)	VIIIa	16.98 (17.10)	-	-
5.	[Cl] Sb(η²-osmab)₂] (0.401g, 0.63mmol) + Na[Al(OPr^i)₄] (0.180g, 0.63mmol)	[(η²-ovmab)₂Sb(μ-OPr^i)₂{Al(OPr^i)₂}] (0.349, 67)	IIIb	12.93 (13.75)	2.91 (3.11)	26.88 (27.31)
6.	[Cl] Sb(η²-osmab)₂] (0.350g, 0.61mmol) + Na[Al(OPr^i)₄] (0.174g, 0.61mmol)	[(η²-osmab)₂Sb(μ-OPr^i)₂{Al(OPr^i)₂}] (0.375, 78)	IVb	15.00 (15.12)	3.17 (3.35)	28.79 (29.35)
7.	[Cl] Sb(η²-osmab)₂] (0.383g, 0.60mmol) + Na[Al(OPr^i)₄] (0.171g, 0.60mmol)	[(η²-osmab)₂Sb(μ-OPr^i)₂ {Al(OPr^i)₂}] (0.341, 68)	VIIIb	13.95 (14.04)	2.96 (3.11)	26.63 (27.25)
8.	[Cl] Sb(η²-ovab)₂] (0.340g, 0.60mmol) + Na[Al(OPr^i)₄] (0.171g, 0.60mmol)	[(η²-ovab)₂Sb(μ-OPr^i)₂] [Al(OPr^i)₂] (0.323, 73.8)	VIIIb	13.95 (14.55)	3.11 (3.22)	28.07 (28.24)

4.4.3 Synthesis of mixed ligand complexes of Aluminium (III) with Schiff bases

To a benzene (~30 cm^3) solution of Na(oiab) (0.232g, 0.95 mmol) and Na(osmab) (0.208g, 0.95 mmol) (0.187g, 0.95mmol) were added hot freshly prepared suspension [(η^2-ovmab)$_2$Al(Cl)$_2$(μ-Cl)$_2$], (0.516g, 0.95 mmol) in benzene-methanol mixture the reaction mixture was refluxed for 4~h during which colour of solution changes from yellow to pinkish black.

The precipitated NaCl(0.116g, 2.85mmol) was removed by filtration the filtrate was concentrated by distillation and stripped off under reduce pressure [(η^2-ovmab)$_2$Al(η^2-oiab) (η^2-osab)]. (0.526g, 81%).

In similar method complexes [(η^2-osnab)Al(η^2-osab)(η^2-oiab)], [(η^2-osmab) (η^2-oiab) Al(η^2-osab)], [(η^2-ovab) (η^2-oiab) Al(η^2-osab)], [(η^2-osaa) (η^2-oiab) Al(η^2-osab)], [(η^2-ovaa) (η^2-oiab) Al(η^2-osab)], [(η^2-onbaph) (η^2-oiab)Al(η^2-osab)] and [(η^2-oinab) (η^2-oiab)Al(η^2-osab)] has been prepared and details are collected in Table [31].

4.4.3.1 Synthesis of Mixed Ligand Complexes of Antimony (III) with Schiff base

Ta benzene (~30 cm^3) solution of Na(oiab) (0.116g, 0.68 mmol) and Na(osab) (0.149g, 0.68 mmol) were added hot (η^2-ovmab)Sb(Cl)$_2$] (0.294g, 0.68 mmol) solution in benzene-methanol mixture the reaction mixture was refluxed for ~5h during which the colour of solution changes from yellow to brown black.

The precipitated NaCl (0.119g, 2.04 mmol) was removed by filtration. The filtrate was concentrated by distillation and stripped off under reduced pressure to afforded reddish black powdered solid [(η^2-ovmab)Sb(η^2-oiab)(η^2-osab)] (0.429g, 81%).

In a similar method complexes [(η^2-snab)(η^2-oiab)Sb(η^2-osab)], [(η^2-osmab)Sb(η^2-oiab)(η^2-osab)], [(η^2-ovab) Sb(η^2-oiab) (η^2-sab)], [(η^2-osaa)(η^2-oiab)Sb(η^2-osab)], [(η^2-ovaa)(η^2-oiab) Sb(η^2-osab)], [(η^2-onbaph)(η^2-oiab)Sb(η^2-osab)] and [(η^2-oinab) (η^2-oiab)Sb(η^2-osab)] has been prepared and details are collected in Table [32].

Table-31

Synthetic and Analytical details for mixed ligand Complexes of Aluminium (III) Containing Schiff bases 1:1:1 molar ratio

Sl. No.	Reactant (g, mmol)			Products (g, % yield)		% Analysis Found (Calcd.) Al
1.	[(µ-Cl)Al₂(CH₃)(η²-omab)] (0.516, 0.95)	+ Na(oiab) (0.232, 0.95)	+ Na(osab) (0.208, 0.95)	[(η²-omab)Al(η²-osab)] (0.526, 81)	(IX)	3.31 (3.94)
2.	[(µ-Cl)Al₂(CH₃)(η²-omab)] (0.452, 0.83)	+ Na(oiab) (0.202, 0.83)	+ Na(osab) (0.181, 0.83)	[(η²-omab)Al(η²-oiab)] (0.437, 77)	(X)	3.28 (3.93)
3.	[(µ-Cl)Al₂(CH₃)(η²-smab)] (0.362, 0.75)	+ Na(oiab) (0.183, 0.75)	+ Na(osab) (0.181, 0.75)	[(η²-smab)Al(η²-oiab)] (0.334, 68)	(XI)	4.03 (4.10)
4.	[(µ-Cl)Al₂(CH₃)(η²-ovnb)] (0.489, 0.95)	+ Na(oiab) (0.232, 0.95)	+ Na(osab) (0.208, 0.95)	[(η²-ovnb)Al(η²-osab)] (0.420, 66)	(XII)	3.84 (4.01)
5.	[(µ-Cl)Al₂(CH₃)(η²-osss)] (0.459, 0.83)	+ Na(oiab) (0.202, 0.83)	+ Na(osab) (0.181, 0.83)	[(η²-osss)Al(η²-osab)] (0.409, 69)	(XIII)	3.18 (3.93)
6.	[(µ-Cl)Al₂(CH₃)(η²-ovaa)] (0.373, 0.63)	+ Na(oiab) (0.151, 0.62)	+ Na(osab) (0.135, 0.62)	[(η²-ovaa)Al(η²-osab)] (0.360, 69)	(XIV)	3.69 (3.75)
7.	[(µ-Cl)Al₂(CH₃)(η²-snbph)] (0.328, 0.75)	+ Na(oiab) (0.183, 0.75)	+ Na(osab) (0.181, 0.75)	[(η²-snbph)Al(η²-oiab)] (0.344, 67)	(XVI)	3.35 (3.91)
8.	[(µ-Cl)Al₂(CH₃)(η²-oiinb)] (0.287, 0.63)	+ Na(oiab) (0.151, 0.62)	+ Na(osab) (0.135, 0.62)	[(η²-oiinb)Al(η²-osab)] (0.317, 72)	(XV)	3.18 (3.78)

Table-32

Synthesis and Analytical details of mixed ligand of Antimony (III) Complexes containing Schiff bases in 1:1:1 molar ratio

Sl. No.	Reactants (g, mmol)			Products (g, % yield)	% Analysis Found (Calcd.) Sb
1.	$[(Cl)_2Sb(\eta^2\text{-ovmab})]$ (0.294, 0.68)	+ Na(oiab) (0.166, 0.68)	+ Na(osab) (0.149, 0.68)	$[(\eta^2\text{-ovmab})Sb(\eta^2\text{-oiab})(\eta^1\text{-osab})]$ (IX) (0.429, 81)	14.30 (15.62)
2.	$[(Cl)_2Sb(\eta^2\text{-osab})]$ (0.338, 0.78)	+ Na(oiab) (0.190, 0.78)	+ Na(osab) (0.170, 0.78)	$[(\eta^1\text{-osab})Sb(\eta^2\text{-oiab})(\eta^2\text{-osab})]$ (X) (0.474, 78)	14.78 (15.60)
3.	$[(Cl)_2Sb(\eta^2\text{-osmab})]$ (0.327, 81)	+ Na(oiab) (0.197, 0.81)	+ Na(osab) (0.177, 0.81)	$[(\eta^2\text{-osmab})Sb(\eta^2\text{-oiab})(\eta^1\text{-osab})]$ (XI) (0.442, 68)	14.39 (15.90)
4.	$[(Cl)_2Sb(\eta^2\text{-ovab})]$ (0.259, 0.62)	+ Na(oiab) (0.151, 0.62)	+ Na(osab) (0.135, 0.62)	$[(\eta^2\text{-ovab})Sb(\eta^2\text{-oiab})(\eta^1\text{-osab})]$ (XII) (0.350, 74)	14.96 (15.90)
5.	$[(Cl)_2Sb(\eta^2\text{-osaan})]$ (0.294, 0.68)	+ Na(oiab) (0.166, 0.68)	+ Na(osab) (0.149, 0.68)	$[(\eta^2\text{-osaab})Sb(\eta^2\text{-oiab})(\eta^1\text{-osab})]$ (XIII) (0.406, 77)	14.78 (15.62)
6.	$[(Cl)_2Sb(\eta^2\text{-ovaa})]$ (0.362, 0.78,)	+ Na(oiab) (0.190, 0.78)	+ Na(osab) (0.179, 0.78)	$[(\eta^2\text{-ovaa})Sb(\eta^2\text{-oiab})(\eta^1\text{-osab})]$ (XIV) (0.422, 67)	14.95 (15.04)
7.	$[(Cl)_2Sb(\eta^2\text{-ombaph})]$ (0.352, 0.81)	+ Na(oiab) (0.197, 0.81)	+ Na(osab) (0.177, 0.81)	$[(\eta^2\text{-ombaph})Sb(\eta^2\text{-oiab})(\eta^1\text{-osab})]$ (XV) (0.489, 73)	15.03 (15.60)
8.	$[(Cl)_2Sb(\eta^2\text{-Oinab})]$ (0.314, 0.68)	+ Na(oiab) (0.166, 0.68)	+ Na(osab) (0.149, 0.68)	$[(\eta^2\text{-Oinab})Sb(\eta^2\text{-oiab})(\eta^1\text{-osab})]$ (XVI) (0.415, 76)	14.98 (15.11)

Chapter-V

SUMMARY

&

REFERENCES

SUMMARY

SUMMARY

The Schiff base metal complexes used in sterioselective polymerization and Aluminium complexes have been used as catalyst for synthesis. The effect Schiff base organometallic complexes on corrosion of mild steel have been investigated, Sulphur donar Aluminium Schiff base metal complexes shows antifertility activity in male albino rats. The Schiff base complexes derive from substituted amino anthraquinones and salicylaldehyde used as there florescence based corrosion indicator.

The use of Antimony in medicine have been reviewed by several worker some organoantimony derivatives showed significant antitumour activity. However dimethylcanthramlde and its analogues have also showed a wide range of biological activity inducing antitumour activity against cancer cell, The Schiff base complexes shows antibacterial and insecticidel activity against cockroach (Periplaneta americana).

A survey of relevant literature on the Schiff base ligands and their metal complexes show that work on main group metal with Schiff base have been carried out only up to bis-tries. A variety of addicts with corresponding trivalent metals have also been reported.

There is no mention any hydrocarbon soluble chloro bridged complexes of main group metal containing Schiff base. The present thesis entitled. "Studies on coordination compounds of some group "13" and "15" elements", deals mainly with synthesis reaction and physico-chemical investigation of some new and novel Aluminium (III) and Antimony (III) complexes of type. $[(Cl)_2M(\eta^2\text{-S.B.})]$

$[(Cl)M(\eta^2\text{-}S.B)_2]$ and $[(S.B.) M (S'.B')(S''.B'')]$ [where M Al(III)and Sb(III) and S.B=schiff Bases{salicylidene -1-aminobenzene (sabH), salicylidene -2-methyl-1-aminobenzene(smabH) vanillidene-2-methyl-1-aminobenzene (vmabH)- salicylidene3-nitro-1-aminobenzene (snabH) vanillidene-1-aminobenzene (vabH), isatidene-3-nitro-1-aminobenzene (iabH) isatin-1-aminobenzene (iabH) salicylidene anthranilic acid (saaH), 4-nitrobenzene xlidene -2-aminophenol (nbaphH) and vanillidene -anthranilic acid (vaaH)} S'.B' (SabH) and S''.B'' (iabH) η^2=number of connectivity sites involved in bonding with metals].

These monochloro complexes have been treated with sodium phenolate [Na(oAr)] and sodium tetraalkoxy aluminate $[Na\{Al(opr^i)\}_4)]$ to produce new phenoxo-bridged complexes $[(\eta^2\text{-}SB)_2m(\mu\ oAr)_2]$ the mixed ligand complexes$[(\eta^2\text{-}SB)_2M(\mu\text{-}opr^i)_2\{Al(opr^i)_2\}]$. All these derivatives have been characterised by elemental analysis, IR Electronic (U.V.-visible) proton ^{1}H NMR, ^{13}C-NMR, FAB-mass to explore the possibility of structural elucidation the content of this thesis have been divided in five chapters.

Chapter-I describes general characteristic of Main group elements, General chemistry of Aluminium, chemistry of Antimony and a brief relevant literature on the metal complexes containing Schiff base as well as recent developments in chemistry of schiff bases having 'N' and 'O' donors atoms.

Chapter-II deals with **"synthesis reactions and physico-chemical studies of Aluminium (III) complexes containing various schiff bases"**. of the types $[(\mu\text{-}Cl)_2Al_2(Cl)_2(\eta^2\text{-}SB)_2]$, $[(\mu\text{-}Cl)_2\ Al_2(\eta^2\text{-}SB)_4]$ and [(S.B.) M $(S'.B')(S''.B'')$ where SB= schiff bases (smabH) (snabH) (vmabH) (vabH) (iabH) (inabH) (saaH) (vaaH) (sabH) (nbaphH) S'.B'=(sabH), S''B''=(iabH) in this chapter, the discussion of the

result optioned by the various studies carried out on the complexes alongwith appropriate conclusion drawn.

During the present course of investigations various complexes of Aluminium (III) have been synthesised, since in most of the cases preparative processes are similar therefore details are given only for representative cases. For the sake of brevity.

Aluminium (III) complexes containing schiff bases vanillidene -2-methyl-1-aminobenzene have been prepared by the reactions of anhydrous Aluminium (III) chloride with sodium salt of schiff bases Na (vamb) Na (snab) in 1:1 and 1:2 molar ratios in benzene-methanol mixture of the types $[(\mu-Cl)_2Al_2(Cl)_2(\eta^2-ovmab)_2]$, $[(\mu-Cl)_2 \quad Al_2(Cl)_2(\eta^2-osnab)_2]$, $[(\mu-Cl)_2Al_2(\eta^2-ovmab)_4]and[(\mu-Cl)_2Al_2(\eta^2-osnab)_4]$ which can be represented by fallowing chemical equations :
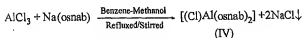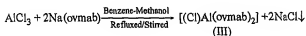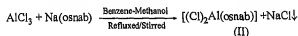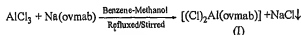
$$AlCl_3 + Na(ovmab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)_2Al(ovmab)] + NaCl\downarrow$$
$$(I)$$

$$AlCl_3 + Na(osnab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)_2Al(osnab)] + NaCl\downarrow$$
$$(II)$$

$$AlCl_3 + 2Na(ovmab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)Al(ovmab)_2] + 2NaCl\downarrow$$
$$(III)$$

$$AlCl_3 + Na(osnab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)Al(osnab)_2] + 2NaCl\downarrow$$
$$(IV)$$

The above complexes are coloured solids and are soluble in common organic solvents such as CHCl$_3$, CH$_3$OH, THF, DMSO, DMF all these complexes have been purified by recrystallisation in C$_6$H$_6$-MeOH in mixture.

The quantitative reactions of mono chloro complexes of Aluminium (III) have been carried out with sodium salt of 4 nitro phenol Na (OAr) and sodium salt of tetraisopropoxyaluminate Na $\{Al(OPr^i)_4\}$ in 1:1 stiochemetric ratio in benzene-methanol mixture which can be represented by following chemical equation :

$$[(Cl)Al(ovmab)_2] + Na(OAr) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(ovmab)_2Al(OAr)] + NaCl\downarrow$$
$$(IIIa)$$

$$[(Cl)Al(osnab)_2] + Na(OAr) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(osnab)_2Al(OAr)] + NaCl\downarrow$$
$$(IVa)$$

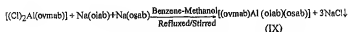$$[(Cl)Al(ovmab)_2] + Na\{Al(OPr^i)_4\} \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(ovmab)_2Al\{Al(OPr^i)_4\}] + NaCl\downarrow$$
$$(IIIb)$$

$$[(Cl)Al(osnab)_2] + Na\{Al(OPr^i)_4\} \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(osnab)_2Al\{Al(OPr^i)_4\}] + NaCl\downarrow$$
$$(IVb)$$
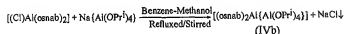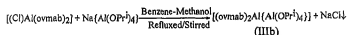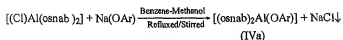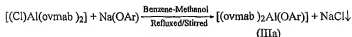
Aluminium (III) mixed ligand complexes of the type $[(SB)Al(S'B')(S''B'')]$ where $S'B' = (sabH)$, $S''B''=(iabH)$ and SB=(vmabH) (vabH) (SmabH) (saaH) (vaaH) (inabH) etc have been synthesised by reaction of freshly prepared dicholoro $[(Cl)_2Al_2(ovmab)]$ with Na(iab) and Na(osab) in 1:1:1 molar ratio in benzene-1-methanol mixture.

$$[(Cl)_2Al(ovmab)] + Na(olab)+Na(osab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(ovmab)Al\ (olab)(osab)] + 3NaCl\downarrow$$
$$(IX)$$

Similar procedure have been adopted for the synthesis of Aluminum (III) complexes containing Schiff bases are summarised. [Table-1].

Table-1

Synthesis Reactions of Aluminium (III) containing various Schiff bases

Sl. No.	Complexes		Product	
1.	AlCl$_3$	+Na(osmab)]	[(Cl)$_2$Al(osmab)]	(V)
2.	AlCl$_3$	+Na(ovab)]	[(Cl)$_2$Al(ovab)]	(VI)
3.	AlCl$_3$	+2Na(osmab)]	[(Cl)Al(osmab)$_2$]	(VII)
4.	AlCl$_3$	+2Na(ovab)]	[(Cl)Al(ovab)$_2$]	(VIII)
5.	[(Cl)Al(osmab)$_2$]	+NaOAr	[(osmab)$_2$Al(OAr)$_2$]	(VIIa)
6.	[(Cl)Al(ovab)$_2$]	+NaOAr	[(ovab)$_2$Al(OAr)$_2$]	(VIIIa)
7.	[(Cl)Al(osmab)$_2$]	+ Na{Al(OPr^i)$_4$]	[(osmab)$_2$Al{Al(OPr^i)$_4$]	(VIIb)
8.	[(Cl)Al(ovab)$_2$]	+ Na{Al(OPr^i)$_4$]	[(ovab)$_2$Al{Al(OPr^i)$_4$]	(VIIIb)
9.	[(Cl)$_2$Al(osan)]	+ Na(oiab) + Na(osab)	[(osaa)Al(oiab)(osab)]	(XIII)
10.	[(Cl)$_2$Al(ovan)]	+ Na(oiab) + Na(osab)	[(ovaa)Al(oiab)(osab)]	(XIV)
11.	[(Cl)$_2$Al(onbaph)] + Na(oiab) + Na(osab)		[(onbaph)Al(oiab)(ossb)](XV)	
12.	[(Cl)$_2$Al(oinab)	+ Na(oiab) + Na(osab)	[(oinab)Al(oiab)(osab)]	(XVI)
13.	[(Cl)$_2$Al(osnab)	+ Na(oiab) + Na(osab)	[(osnab)Al(oiab)(osab)]	(X)

The IR spectra of Schiff base indicated by the presence of absorption band at 1625-1614 cm^{-1} in free ligands, which is characteristic for $\nu_{(C=N)}$ band, in the complexes. The band shifted towards lower wave number at 1614-1595cm^{-1} indicates coordination of azomethine nitrogen with metal ion.

The Schiff bases generally containing (Phenolic group) displays two band ~3564-3329 cm^{-1} and at 1398-1310 cm^{-1} which have been specified for $\nu_{(O-H)}$ stretching and $\delta_{(O-H)}$ deformation frequencies respectively. These frequencies disappeared in the spectra of complexes of Aluminium (III) suggesting deprotonation of phenolic OH after chelation with metal ion.

$\nu_{(C-O)}$ phenolic bands were obtained at 1277-1266 which shifted in higher region at 1293-1270 cm^{-1} in complexes suggest phenolic oxygen involved in bonding.

In monochloro Aluminium (III) complexes, the terminal chloride $\nu_{t(Al-Cl)}$ stretching frequency usually occurs at higher region 345-310 cm^{-1} than the bridging metal chloride $\nu_{b(M-Cl)}$ stretching frequencies, which occurs in the lower region ~190-295 cm^{-1} due to delocalization of electrons in chelate ring. These complexes (III, IV, VII, VIII) having no sharp band in the range 345-310cm^{-1} confirms absence of terminal chlorine atom show the strong band in the region 190-295 cm^{-1} and identified for ν_{Al-Cl} stretch for bridging chlorine. On the basis of above finding following representative structure have been suggested.
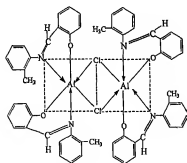
Fig. 1 Proposed structure of [(μ-Cl)$_2$Al$_2$(η^2-osmab)$_4$]

In the dichloro complexes (I, II, IV, V) showed strong band in the region 345-310 cm^{-1} and 190-295 cm^{-1} give information that it contain both terminal and bridging chlorine. On the basis of these studies following representative structures have been suggested.
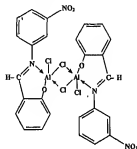
Fig.-2 : Proposed structure of $[(\mu\text{-Cl})_2Al_2(Cl)_2(\eta^2\text{-osnab})_2]$

The IR spectra of Phenoxo-bridge complexes (IIIa), (IVa), (VIIa), (VIIIa). The $\nu_{(C-O)}$ band appeared at 1277-1269 cm^{-1} in free ligand shifted to higher frequency region (by~11-21 cm^{-1}) in complexes assigned to $\nu_{(C-O)}$ (phenolic) stretch of phenxo group.
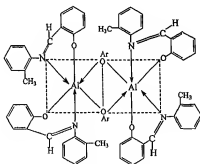
Fig.-3: Proposed structure of $[(\mu\text{-OAr})_2Al_2(\eta^2\text{-osnab})_4]$

The IR spectra of alkoxo-bridged [130-134] complexes(III-b), (IV-b), (VII-b), (VIII-b), exhibited characteristic frequency for metal alkoxy group $v_{(Al-O-Al)}$ for which band observed in the region 735-751 cm^{-1}. The strong intensity band observed in the region 1015-1025 cm^{-1}, which may be specified for $v_{(C-O)}$ of bridging and terminal isopropoxy groups.

All the complexes shows characteristic IR frequency in the range 610-587 cm^{-1} which may be assigned to Al-O vibration the band 475-450 cm^{-1} observed in the Aluminium complexes may be attributed to $v_{(Al-N)}$ vibration.

The electronic spectra of Schiff bases exhibit three bands around 40000, 31746 and 25000cm^{-1}. The band around 40000 and 31746 cm^{-1} are probably due to π - π^* transitions of benzenoid ring are conjugated with double bond of azomethine group and the band around 25000 cm^{-1} may be due to the n→π^*, transition of bonding electrons present in the azomethine group in the Aluminium(III) complexes. There is no shift in the position of first two bands. These bands in complexes are slightly broader in nature probably due to presence of two different types of Schiff bases. The band around 25000 cm^{-1} shows bathochromic shifts in between 25000-23800 in the complexes due to the coordination of nitrogen of azomethine group with central Aluminium atom. Details are summarized in Table [09].

The proton magnetic resonance spectra of these complexes recorded in CDCl$_3$ and in DMSO-d$_6$ the spectra lead to the following conclusions :

(i)   A strong signal appearing in the region δ13.6-13.8 ppm may be assigned to OH proton of Schiff base, however this signal may

disappear in the spectra of corresponding Aluminium complexes showing, that deprotonation of OH subsequently involved in the Al-O bond formation.

(ii) The proton signal appearing in the region $\delta 8.10$ ppm in free ligand due to azomethine proton this signal shifted down field in Aluminium (III) complexes from $\delta 8.10$ to 9.25 ppm. These data may provide support that azomethine nitrogen involved in bonding.

(iii) The chemical shift due to aromatic ring proton appears in between 7.8-8.4 ppm in ligands which may be shifted slightly down field in the complexes may be due to decrease in electron density after formation of complex.

(iv) Vanillidene Schiff bases showed an extra proton signal due to m-OCH$_3$ group in complexes (I, III, IIIa, IIIb, IV, VII, VIIIa, VIIIb, IX, XII, XIV) observed near $\delta 3.50$-3.90 ppm.

(v) A doublet obtained at $\delta 11.2$ ppm in the spectra of isatin derived ligand which may be disappeared in the complexes (IX, X, XI, XII, XIII, XIV, XV, XVI), further confirming enolization of Keto group and Al-O band formation occurred.

(vi) The methine protons of terminal and bridging isopropoxy group are observed in complexes (IIIb, VIb, VIIb, VIIIb) at $\delta 3.90$ to 3.99 ppm. and $\delta 4.06$ to 4.25 ppm respectively. This data may suggests that two Aluminium atom are bonded with each other through isopropoxy bridged structure.

(vii) The signal due to other protons in Schiff bases and their shift in their corresponding Aluminium (III) are compatible with

literature data. On the basis of above studies following structure will be assigned :
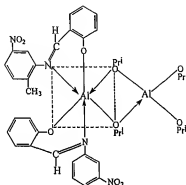
Fig.-4: Proposed structure of [(η²-osnab)₂Al(μ-OPrⁱ)₂Al{(OPrⁱ)₂}]

(i)   The ligand ^{13}C NMR studies showed reasonable shift in the phenolic carbon from δ149.84 to 159.64 ppm. The down field shift in phenolic carbon atom showing coordination may occures from oxygen and form Al-O bond.

(ii) The Schiff bases showed sharp singlet at δ151.24 ppm for azomethine carbon atom, which may shifted down field in the complexes δ160.15 ppm showing coordination of azomethine nitrogen with Aluminium (III) atom.

(iii) In Aluminium (III) complexes signal appeared in the region δ125.62, 138.50, 122.70 ppm, which may be assigned to the three different carbon atom of benzene ring of ligand moiety. There is no appreciable shift found in the carbon of benzene ring.

(iv) In the ^{13}C NMR spectral data of ligand (Isatine derivative) and their complexes (IX, X, XI, XII, XIII, XIV, XV, XVI). The down field shift in the position of amido carbon from $\delta 166$ to $\delta 170$ ppm clearly indicated that covalent bond formation may occur through enolic form of ligand.

(v) A sharp signal obtained for methine carbon of the terminal and bridging isopropoxy groups are observed in complexes (IIIb, VIb, VIIb, VIIIb) at $\delta 60.18$ to 60.52 ppm and $\delta 61.16$ to 64.42 ppm respectively. These data may suggest that two Aluminium atoms are bonded to each other through isopropoxy bridged carbon atom.

(vi) A sharp singlet showed downfield shift due of -COOH carbon atom from $\delta 170$ to 162 ppm in comparison to free ligand which indicated that coordination may occur through carboxy oxygen in monodentate fashion :.

(vii) Vanillidene Schiff bases Aluminium (III) complexes (I, III, IIIa, IIIb, IV, VII, VIIIa, VIIIb, IX, XII, XIV) shows singlet at $\delta 54.1$ ppm, which is characteristic of OCH_3 group.

The FAB-mass spectral studies of dichloro Aluminium (III) complexes such as $[(\mu-Cl)_2Al_2(Cl_2)(\eta 2\text{-ovmab})_2]$ showed characteristic molecular ion $[M^+]$ peak at $m/z = 676.60$ which correspond to the molecular weight of the compound, another peak obtained at $m/z = 238.31$ indicated the fragmentation of dimer to monomer. Beside these other fragmentation peak obtained indicating the fragmentation of ligand from monomer by the formation of radical cation.

The FAB-mass spectral studies of monochloro Aluminium (III) complexes $[(\mu-Cl)_2Al_2(\eta^2\text{-osnab})_4]$ showed characteristic molecular ion peak at m/z 1089, which correspond to molecular weight of compound, another peak obtained at m/z = 544 confirms fragmentation of dimer to monomer besides these other peak may be obtained due to fragmentation of ligand moiety from monomer.

The FAB-mass spectral studies of mixed ligand complexes $[(\mu-Cl)_2Al_2(\eta^2\text{-osnab})_4]$ showed characteristic molecular ion [M⁺] peak at m/z = 684 which correspond to molecular weight of compound, suggest monomeric nature of the complex.

Chapter III- deals with "Synthesis reactions and Phyicochemical Studies of Antimony (III) complexes containing various Schiff bases", of the type $[(Cl)_2Sb(\eta^2\text{-S.B.})]$ $[(Cl)Sb(\eta^2\text{-Sb})^2]$ where S.B. = Schiff base (vmabH, vabH, snabH, saaH, vaaH, nabH, nbaphH smabH) and $[(SB)Sb(S'B')(S''B'')]$ where S'B' = iabH and S''B'' = (sabH).

A hot solution of anhydrous $SbCl_3$ in benzene was added slowly to a freshly prepared, Sodium salt of vanillidene-2-methyl-1-aminobenzene (vmabH) and Salicylidene-3-nitro-1-amino benzene in 1:1 and 1:2 molar ratios, to afforded complexes of the type $[(Cl)_2Sb(\eta^2\text{-ovmab})]$, $[(Cl)_2Sb(\eta^2\text{-osnab})]$, $[(Cl)_2Sb(\eta^2\text{-omab})]$ and $[(Cl)_2Sb(\eta^2\text{-osnab})]$ which can be illustrated by following chemical equations :
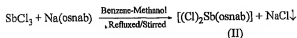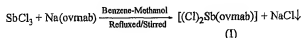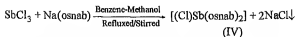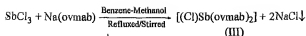
$$SbCl_3 + Na(ovmab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)_2Sb(ovmab)] + NaCl\downarrow$$
$$(I)$$

$$SbCl_3 + Na(osnab) \xrightarrow[\text{,Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)_2Sb(osnab)] + NaCl\downarrow$$
$$(II)$$

$$SbCl_3 + Na(ovmab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)Sb(ovmab)_2] + 2NaCl\downarrow$$
$$(III)$$

$$SbCl_3 + Na(osnab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(Cl)Sb(osnab)_2] + 2NaCl\downarrow$$
$$(IV)$$

The above complexes are coloured solid and are soluble in common organic solvents, such as CH_3OH, CCl_4, $CHCl_3$, and DMSO etc. All these complexes have been purified by recrystallisation in Benzene-methanol mixture.

The quantitative reaction of monochloro complexes of Antimony(III) have been carried out with sodium salt of 4-nitrophenol Na(OAr) and sodium salt of tetraisopropoxy aluminate $Na\{Al(OPr^i)_4\}$ in 1:1 stoichiometric ratio in benzene-methanol mixture, which can be represented by following chemical equations.

$$[(Cl)Sb(ovmab)_2] + Na(OAr) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(ovmab)_2Sb(OAr)] + NaCl,$$
$$(IIIa)$$

$$[(Cl)Sb(osnab)_2] + Na(OAr) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(osnab)_2Sb(OAr)] + NaCl\downarrow$$
$$(IVa)$$

$$[(Cl)Sb(ovmab)_2] + Na\{Al(OPr^i)_4\} \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(ovmab)_2Sb\{Al(OPr^i)_4\}] + NaCl\downarrow$$
$$(IIIb)$$

$$[(Cl)Sb(osnab)_2] + Na\{Al(OPr^i)_4\} \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(osnab)_2Sb\{Al(OPr^i)_4\}] + NaCl\downarrow$$
$$(IVb)$$
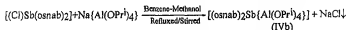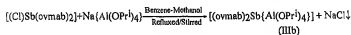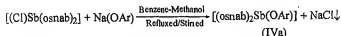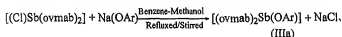
It is important to mention that alkoxo-bridged complexes undergoes decomposition on heating under reduced pressure the distillate $\{Al(OPr^i)_3\}$ could be identified by elemental analysis.

$$[(Cl)Sb(\eta^2\text{-osmab})_2] + Na\{Al(OPr^i)_4\} \xrightarrow[-275^\circ]{\Delta} 2\{Al(OPr^i)_3\}\}\uparrow + [\{Sb(OPr^i)_2\}] + [Sb(osnab)_2$$

$[(Cl)Sb(\eta^2\text{-ovab})_2] + Na[Al(OPr^i)_4] \xrightarrow[\Delta]{275°} 2[{Al(OPr^i)_3}]\uparrow + [{Sb(OPr^i)_2}] + [Sb(ovab)_2]$
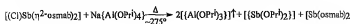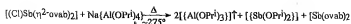
Antimony (III) mixed ligand complexes of the type $[(\eta^2\text{-}ovmab)Sb(\eta^2\text{-oiab})(\eta^2\text{-osab})]$ have been synthesised by reaction of dichloro complexes $[(Cl)_2Sb(ovmab)]$ with Na(oiab) and Na(osab) in 1:1:1 molar ratio in benzene methanol mixture.

$[(Cl)_2Sb(ovmab) + Na(oiab)+Na(osab) \xrightarrow[\text{Refluxed/Stirred}]{\text{Benzene-Methanol}} [(ovmab)Sb(oiab)(osab)] + 3NaCl\downarrow$

$\hspace{8cm}$ (IX)

Similar method have been adopted for synthesis of Antimony (III)complexes and details are summarised in table-2.

Table-2

Synthesis Reactions of Aluminium (III) containing Schiff bases

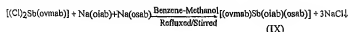| Sl. No.	Complexes		Product	
1.	SbCl$_3$	+Na(osmab)]	[(Cl)$_2$Sb(osmab)]	(V)
2.	SbCl$_3$	+Na(ovab)]	[(Cl)$_2$Sb(ovab)]	(VI)
3.	SbCl$_3$	+2Na(osmab)]	[(Cl)Sb(osmab)$_2$]	(VII)
4.	SbCl$_3$	+2Na(ovab)]	[(Cl)Sb(ovab)$_2$]	(VIII)
5.	[(Cl)Sb(osmab)$_2$]	+NaOAr	[(osmab)$_2$Sb(OAr$_2$)]	(VIIa)
6.	[(Cl)Sb(ovab)$_2$]	+NaOAr	[(ovab)$_2$Sb(OAr$_2$)]	(VIIIa)
7.	[(Cl)Sb(osmab)$_2$]	+ Na[Al(OPr^i)$_4$]	[(osmab)$_2$Sb{Al(OPr^i)$_4$}]	(VIIb)
8.	[(Cl)Sb(ovab)$_2$]	+ Na(Al(OPr^i)$_4$	[(ovab)$_2$Sb{Al(OPr^i)$_4$}]	(VIIIb)
9.	[(Cl)$_2$Sb(osan)]	+ Na(oiab) + Na(osab)	[(osaa)Sb(oiab)(osab)]	(XIII)
10.	[(Cl)$_2$Sb(ovna)]	+ Na(oiab) + Na(osab)	[(ovaa)Sb(oiab)(osab)]	(XIV)
11.	[(Cl)$_2$Sb(onbaph)] + Na(oiab) + Na(osab)		[(onbaph)Sb(oiab)(osab)]	(XV)
12.	[(Cl)$_2$Sb(Oinab)]	+ Na(oiab) + Na(osab)	[(oinab)Sb(oiab)(osab)]	(XVI)

The presence of Schiff base moieties indicated by the appearance of absorption band at 1648-1618 cm^{-1} in ligands is characteristic for $\nu_{C=N}$ in the complexes shifting of $\nu_{C=N}$ band to lower wave number at 1595-622 cm^{-1} indicates coordination of azomethine nitrogen with metal ion.

The Schiff bases generally containing phenolic group two IR bands observed at ~3564-3329 cm^{-1} and at 1389-1310 cm^{-1}, which have been specified for ν_{OH} stretching and ν_{OH} deformation frequencies respectively. These frequencies disappeared in the spectra of Antimony (III) complexes suggesting deprotonation of phenolic OH after chelation with metal ion.

The $\nu_{(C-O)}$ phenolic band were observed at 1277-1266 cm^{-1} in all the Schiff bases. These bands shifted to higher wave number (1293-1270) cm^{-1} confirm about the taking place coordination through phenolic oxygen.

The dichloro and monochloro complexes(I), (II), (III), [(Cl)Sb(η^2-osnab)$_2$](IV), (V),(VI), (VII) and (VIII) displayes sharp IR bands characteristic absorption frequency in the region 350 cm^{-1} assigned for $\nu_{(Sb-Cl)}$ metal-chlorine stretching frequency. On the basis of above finding following representative structure have been suggested.
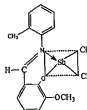
Fig.-5 Proposed Structure of [(Cl)$_2$Sb(η^2-ovmab)]

The infrared spectra of phenoxo containing, complexes (IIIa) and (IVa) (VIIa) and (VIIIa), the $\nu_{(C-O)}$ frequency of free ligand obtained at 1272-1266 cm^{-1} this band shifted (11-21) cm^{-1} higher region in complexes assigned to bond formation.

Fig.-6: Proposed Structure of [(Cl)$_2$Sb(η^2-osmab)]

Stretch of phenoxo group. This data is confirming that bonding may occurs from phenolic oxygen. On the basis of above finding following structure may be proposed.

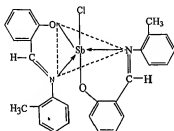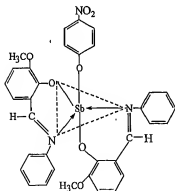**Fig.-7: Proposed Structure for [(OAr) Sb(η^2-ovab)$_2$]**

The infrared spectra of alkoxy bridged complexes (IIIb), (IVb), [(η²-(VIIb) and(VIIIb) showed characteristic strong intensity band in the region 1025-1015 cm⁻¹ which may be specified for $v_{(C-O)}$ terminal alkoxy group and for bridging alkoxy group 751-735 cm⁻¹.

In the complexes two bands appeared at 580 cm⁻¹ and 540 cm⁻¹ are assigned to $v_{(Sb-N)}$ vibrations. This data suggest the possible trans configuration for two ligand molecules around Antimony(III). However, a band found at approximately 530 cm⁻¹ which characterises cis. environment of ligand around metal.

The electronic spectra of schiff base Antimony(III) complexes exhibited three bands around 44.802, 37202 and 29620 possible due to π–π* transition of benzenoid ring in conjugation with double bond of azomethine group. The bond around 25000 cm⁻¹ may be due to n–π* transition of bonding electron present in the nitrogen of azomethine group in the corresponding Antimony(III) complexes. There is no shift in the position of first two bands. These bands in the complexes are slightly broader in nature due to presence of two different type of Schiff bases in the complexes. The ligand bands showed bathochromic shift in the complexes this may be due to coordination of azomethine nitrogen with central Antimony(III) atom.

The proton magnetic resonance spectra of these complexes due recorded in CDCl₃ and DMSO-d₆. The spectra of complexes can lead to the following conclusions :

(i)   A strong signal appeared in the region 13.6-13.8 ppm may be assigned to OH proton of Schiff bases, however this signal may disappeared in the spectra of corresponding Antimony(III)

complexes, indicating the deprotonation of OH and Sb–O bond formation may occurs.

(ii) The proton signal appeared in the region $\delta 8.10$ ppm in free ligand due to azomethine proton. This signal shifted down field in Antimony (III) complexes from $\delta 8.10$ to 9.25 ppm.

(iii) The chemical shift due to aromatic ring protons appeared at $\delta 7.8$-8.4 ppm in ligands which may be shifted slightly down field in the complexes may be due to decrease in electron density after formation of complex.

(iv) Vanillidene Schiff base showed an (I, III, IIIa, IIIb, IV, VII, VIIIa, VIIIb, IX, XII, XIV) extra proton signal due to m-OCH$_3$ group at $\delta 3.50$-3.90ppm.

(v) A singlet due to NH obtained at $\delta 11.2$ ppm in the spectra of isatin derived ligands which may be disappeared in the complexes (IX, X, XI, XII, XIII, XIV, XV, XVI) further confirming enolization of keto group and coordination may occur through oxygen.

(vi) The methine proton of terminal and bridging isopropoxy groups are observed at $\delta 3.90$-399 ppm and $\delta 4.06$-4.25 ppm respectively. The data may suggests that Antimony (III) banded (IIIb, VIb, VIIb, VIIIb) with tetraalkoxy aluminate through isopropoxy bridged structure.
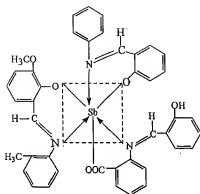
Fig -8: Proposed structure of mixed ligand complexes
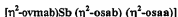
[η²-ovmab)Sb (η²-osab) (η²-osaa)]

The ^{13}C NMR spectra of these complexes due recorded in CDCl$_3$ and DMSO-d$_6$. The spectra of complexes can lead to the following conclusions :

(i)   The ^{13}C NMR studies of ligands shows reasonable shift in the phenolic carbon from δ149.84 to 159.64 ppm.. The downfield shift in phenolic carbon atom showed invlved in coordination(2)

(ii) The Schiff bases showed singlet at δ151.24 ppm for azomethie carbon atom which may shifted downfield δ160.15 ppm showing coordination of azomethine nitrogen

(iii) The ^{13}C signal appeared the region δ125.62, 138.50 and 122.70 ppm may be assigned to the three different carbon atoms of the

benzene ring of ligand. There is no appreciable shift found in the carbon atom of benzene ring.

(iv) In the ^{13}C NMR spectral data of ligands (isatin derived) and their complexes, (IX, X, XI, XII, XIII, XIV, XV, XVI) the appreciable downfield shift in the position of amido carbon from δ166 to 170 ppm clearly indicate that covalent (Sb-O) bond formation may occur due to enolic form of ligand.

(v) A sharp signal obtained for the methine carbon of the terminal and bridging isopropoxy groups are observed in complexes (IIIb, VIb, VIIb, VIIIb) at δ60.18 to 60.52 ppm and δ61.16 to 64.42 ppm respectively may suggesting that Antimony and Aluminium atoms are bonded to each other with isopropoxy bridged carbon atom.

(vi) A sharp singlet showed downfield shift of -COOH carbon atom [50] from δ170 to 162 ppm in comparison to free ligand showing that coordination (XIII, XIV), may occur through carboxyl oxygen in monodentate way.

(vii) Vanillidene Schiff base complexes of Antimony (III) showed (I, III, IIIa, IIIb, IV, VII, VIIIa, VIIIb, IX, XII, XIV) a singlet at δ54.1 ppm which is characteristic of m-OCH$_3$ group.

Fig.-9 : Proposed structure of [(η²-osmab)₂Sb(μ-OPrⁱ)₂ {Al(OPrⁱ)₂}]

The FAB-mass spectrum of representative complex of dichloro such as [(Cl)₂Sb(η²-osmab)] showed characteristic molecular ion [M⁺] peak at m/z = 403 correspond to the molecular weight of complex suggesting monomeric nature of the complexes.

The FAB-mass spectrum of monochloro complexes [(η²-ovab)₂Sb(Cl)] exhibited molecular ion [m⁺] peaks at m/z = 609 suggested monomeric nature of the complexes.

The Fab-mass spectrum of mixed ligand complexes of the type [(η²-ovmab)Sb(η²-osab)(η²-oiab)] exhibited molecular ion peak [M⁺] at m/z 7.79 suggesting monomeric nature of the complexes.

Chapter IV in corporate description of the methods & materials employed in the present investigations, followed by brief experimental details of individual experiments.

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List of Publications

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Research Papers

Presented in Various

Conferences

of Publications and Research Papers Presented in
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A) List of Publications

(1) Synthesis and Structural Studies of some mixed ligands (Schiff bases) complexes of Al(III) and Sb(III). Communicated (2005). (Main Group Metal Chemistry).

(2) Synthesis and Spectroscopic Studies of some new Derivatives containing Aluminium (III) atoms in Different (4,5,6) coordination states. [Under Communication (2005)].

(3) Synthesis Reactions and Spectral Characterization of mono and dichloro Schiff base complexes of antimony(III). [Under communication (2005)].

B) List of Papers presented in Various Conferences:

(1) Synthesis and spectroscopic [IR, (U.V.-visible), ^{1}H, ^{13}C NMR and FAB-mass] studies of mixed ligand complexes of Aluminium (III) R.K. Dubey and Rajnish Rai.

(The Conference of the International Academy of Physical Sciences 21-23 Dec. 2004).

(2) Synthesis and phyco-chemical studies of aluminium (IV) chloride complexes containing bidentate Schiff bases R.K. Dubey, Rajnish Rai. (Seminar held at (18-20 Dec) I.C.C. Indian Council of Chemistry 2005 (18-20 Dec 2005) held BIT, Meshra Ranchi (Jharkhand) to be presented.)